AUTHOR QUERY FORM

American Institute of Physics	Journal: J. Appl. Phys. Article Number: 099209JAP	Please provide your responses and any corrections by annotating this PDF and uploading it to AIP's eProof website as detailed in the Welcome email.

Dear Author,

Below are the queries associated with your article; please answer all of these queries before sending the proof back to AIP. Author please indicate the correct color processing option from the list below:

1. Author, please confirm Figure number(s) that should appear as color in print. Please know that any associated mandatory fees will apply for figures printed in color.
2. Author, please confirm Figure number(s) that should appear as color online only, there will be no fees applied.
3. Author, your paper currently does not include any color figures for online or print. If color is needed please indicate which figures it should be applied to and whether it is color in print or online.

Location in article	Query / Remark: click on the Q link to navigate to the appropriate spot in the proof. There, insert your comments as a PDF annotation.
AQ1	Please rephrase the sentence "Silicon is an opaque material…" for clarity.
AQ2	Please check and confirm the edits made in the sentence "Meanwhile, these bubbles…."
AQ3	Please provide DOI number for Refs. 9, and 14.

Thank you for your assistance.

JOURNAL OF APPLIED PHYSICS **111**, 000000 (2012)

High-aspect-ratio grooves fabricated in silicon by a single pass of femtosecond laser pulses

Yuncan Ma (马云灿), Haitao Shi (史海涛), Jinhai Si (司金海),[a)] Hai Ren (任海), Tao Chen (陈涛), Feng Chen (陈烽), and Xun Hou (侯洵)
Key Laboratory for Physical Electronics and Devices of the Ministry of Education & Shaanxi Key Laboratory of Information Photonic Technique, School of Electronics and Information Engineering, Xi'an Jiaotong University, Xianning West Road 28, Xi'an 710049, China

(Received 17 November 2011; accepted 29 March 2012; published online xx xx xxxx)

High-aspect-ratio grooves have been fabricated in silicon by a single pass of femtosecond laser pulses in water and ambient air. Scanning electron microscopy and energy dispersive x-ray spectroscopy were employed to image for the morphology of the photoinduced grooves and analyze the chemical composition in the surrounding of the grooves. It was observed that the sidewall of the grooves fabricated in water was much smoother than that in ambient air, and there were homogeneous nano-scale protrusions on the sidewall of the grooves fabricated in water. Meanwhile, oxygen species, which was incorporated into the grooves fabricated in air, was not observed in those in water. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4709726]

I. INTRODUCTION

Femtosecond laser pulses have proved to be an effective tool for processing a wide range of materials, such as semiconductor,[1] glass,[2] polymer,[3] ceramic,[4] and metal.[5]. Because silicon is one of the most commonly used materials in semiconductor industry, femtosecond laser interaction with silicon has attracted growing attention owing to the possible applications of the microstructures fabricated on silicon surface in silicon-based microelectronics and microelectromechanical devices. Various structures, such as craters,[6,7] ripples,[8–10] columns,[11–13] and nanofibrous structures,[14] have been produced on silicon surface after irradiation with femtosecond laser pulses. However, as the wavelength of the light in most experiments is in the absorption region of silicon, and the observation of the microstructures inside silicon is not so convenient as those fabricated in transparent materials, the studies of femtosecond laser interaction with silicon mainly restricted to the surface; few investigations have been conducted inside silicon. Recently, we reported the photoinduced single and multiple microchannels inside silicon wafer by femtosecond laser pulses at the wavelength of 800 nm, which is located at the absorption region of silicon.[15–17]

The grooves in silicon have attracted more and more interest due to its potential applications in optical control over surface-plasmon-polariton-assisted THz transmission.[18] Several studies have been conducted on the fabrication of grooves in silicon by cw laser[19–21] or femtosecond laser,[22] and the high aspect ratio was achieved by means of multiple passes of the incident laser[22] or using high-repetition-rate laser.[23] Even so, we predict that the aspect ratio or quality of the grooves could be further improved by using the femtosecond laser microfabrication technology within silicon or choosing appropriate environments. Furthermore, the chemical composition in the surrounding of the grooves needs to be further confirmed.

In this paper, high-aspect-ratio grooves are fabricated in silicon in de-ionized water and ambient air by a single pass of femtosecond laser pulses. In our experiment, the femtosecond laser microfabrication technology within silicon was employed to fabricate the high-aspect-ratio grooves in which the laser beam was focused below the surface of the silicon wafer. The morphology and chemical composition of the induced grooves were characterized by a scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS), respectively. Meanwhile, the oxygen species, which was not found in the surrounding of the grooves fabricated in de-ionized water, was incorporated into the grooves in ambient air. These results indicated that the incorporation of oxygen into the fabricated microstructures could be effectively eliminated in de-ionized water environment.

II. EXPERIMENTAL DETAILS

An amplified Ti: sapphire femtosecond laser system (FEMTOPOWER Compact Pro, Austria) was employed to provide laser pulses with 30-fs pulse duration, 800-nm wavelength, and 1-KHz repetition rate. The energy of the incident laser pulses could be continuously varied by rotating a variable neutral density filter (NDF), and the access of the laser was controlled via a mechanical shutter.

Figure 1 shows the schematic illustration for the fabrication of the grooves in de-ionized water. The silicon wafer with a thickness of 300 μm was previously rinsed in an ultrasonic cleaner with absolute alcohol and de-ionized water for about 10 min; then it was fixed horizontally in an open glass container filled with water. The container was mounted on a computer controlled three-dimensional translating stage with a resolution of 40 nm at x, y, and z axis. The distance between the silicon surface and the water surface was estimated to about 1 mm. In addition, when the silicon wafer was irradiated in ambient air, the glass container was moved away and the wafer was mounted horizontally on the translating stage. No matter the silicon wafers were immersed in

[a)]Author to whom correspondence should be addressed. Electronic mail: jinhaisi@mail.xjtu.edu.cn. Tel.: +86 029 82663485.

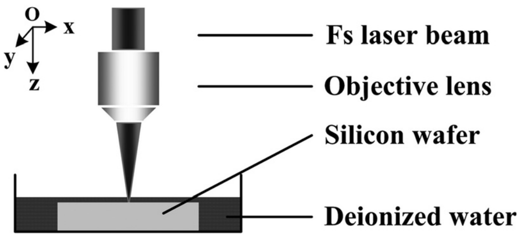

FIG. 1. Schematic illustration for the fabrication of the grooves in de-ionized water.

de-ionized water or ambient air, a 50× microscope objective with the numerical aperture (NA) of 0.50 was employed to focus the femtosecond laser pulses below the surface of silicon wafers (about 25 μm with regard to the silicon surface). The focal plane was determined by finding the smallest diameter of the photoinduced craters via the irradiation of the silicon wafers at different *z* positions. Furthermore, the scanning direction was set parallel to *y* axis, which was parallel to the polarization direction of the incident laser.

After irradiation with the femtosecond laser pulses, surface damage lines could be observed clearly on the surface of the silicon wafer via a CCD camera connected to a computer. The irradiated silicon wafers were polished with waterproof abrasive paper along the cross section (means the *xoz* plane) which was perpendicular to the scanning direction (means the *y* axis direction) to a random position to observe the induced grooves in silicon wafers. After that, the silicon wafers were rinsed with de-ionized water and absolute alcohol in ultrasonic cleaner for about 15 min. Finally, the photoinduced grooves and chemical composition were characterized by SEM equipped with EDS (JEOL JSM-6390A series).

III. RESULTS AND DISCUSSION

First, the grooves were produced in de-ionized water. The laser average energy was set at 5.0 mW, and the scanning speeds of the laser were set at 5 μm/s, 10 μm/s, and 15 μm/s. ~~Silicon is an opaque material, the observation of microstructures formed in which is not so convenient as that in transparent materials; therefore, the irradiated silicon wafer was polished by waterproof abrasive paper to a random position to observe the fabricated grooves from the cross section, which also suggests the continuity of the induced grooves in silicon as well along the scanning direction.~~

Figure 2 illustrates the SEM images of the grooves fabricated in de-ionized water at different scanning speeds. For each experimental condition, ten grooves were produced in different locations at a certain interval of 50 μm in silicon along *x* axis, and the measurement in width and depth of the grooves under the same condition suggest that the repeatability of the geometry of the grooves is guaranteed. We can see from Fig. 2 that the grooves extend to the interior of the silicon wafer about 30 μm (at the speed of 10 μm/s), the width of the grooves is estimated to about 1 μm, meaning the aspect ratio of the grooves is 30. From Fig. 2, we can also see that the width of the grooves remains almost constant for different scanning speeds, while the depth of the grooves decreases with the increase of the scanning speed. This is

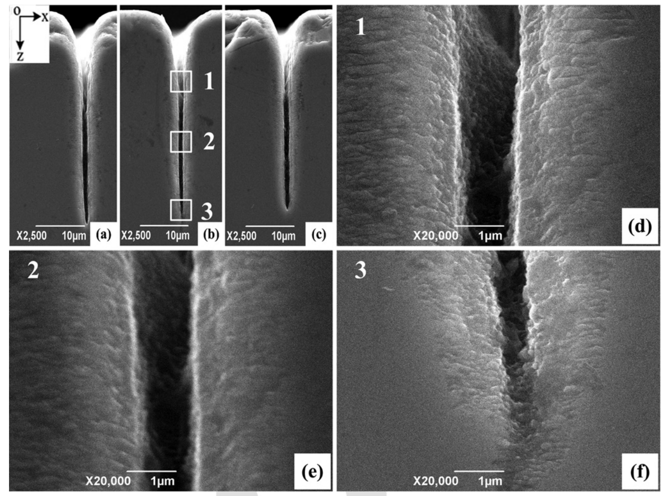

FIG. 2. SEM images of grooves fabricated in de-ionized water under different scanning speeds: (a) 5 μm/s; (b) 10 μm/s; (c) 15 μm/s. The laser power was set at 5.0 mW. The magnified morphology of the area marked out in (c) was illustrated in (d), (e), and (f).

because the laser energy accumulated in unit area of the silicon sample decreases with the increase of the scanning speed, which makes the ablation efficiency of silicon decrease, consequently the depth of the grooves decreases.

In order to compare the morphology of the grooves formed in different environments, we produced grooves in ambient air under the following laser parameters: the laser average energy was set at 5.0 mW, the scanning speed was set at 5 μm/s. The induced grooves are shown in Fig. 3. We can see from Fig. 3(a) that the depth of the induced grooves is about 100 μm, while the width of the grooves is estimated to about 4 μm, meaning the aspect ratio of the grooves is 25, which is also much larger than those of the grooves induced in silicon[19–22] in the same environment. In our experiment, the high-aspect-ratio grooves were produced by a single pass of tightly focused femtosecond laser pulses, which improved the efficiency of producing grooves in silicon.

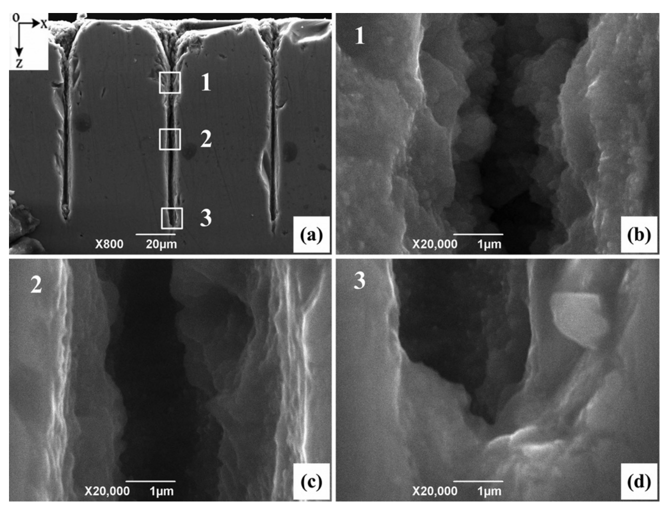

FIG. 3. SEM images of the grooves fabricated in ambient air. The laser average power was 5.0 mW, and the scanning speed was 5 μm/s. The magnified morphology of the area marked out in (a) was illustrated in (b), (c), and (d).

By comparing the morphology of the grooves at different positions of grooves fabricated in water (in Fig. 2) and ambient air (in Fig. 3), it is observed that the grooves fabricated in de-ionized water are much smoother than those in ambient air. Moreover, there are homogeneous nano-scale protrusions on the sidewall of the grooves in de-ionized water, and the order of magnitude of the protrusions is estimated to 100 nm. When intense femtosecond laser irradiated the silicon wafer immersed in water, high-intensity plasmas were produced near the focal volume, and lots of cavitation bubbles formed due to the expansion of these plasmas, which is similar to the laser-induced breakdown in water.[24,25] These bubbles were not stable in water, they would ascend to the surface, and the induced debris was taken away from the silicon substrate by these bubbles. Meanwhile, these bubbles might lead to defocusing or scattering of subsequent pulses ~~and~~ therefore reduced the ablation efficiency of silicon, which results in the depth of the grooves fabricated in water being ~~shallower~~ than ~~that~~ in ambient air. When the femtosecond laser pulses irradiated the silicon wafer in ambient air, the debris induced by the previous femtosecond laser pulses remained near the damage area. Therefore, the grooves fabricated in de-ionized water were much smoother than those in ambient air.

Finally, we analyzed the chemical composition in the surrounding of the grooves by employing the EDS in the converse and longitudinal direction. The measured regions are marked out in Figs. 4(a) and 5(a), and the results are illustrated in Figs. 4(b) and 4(c) and 5(b) and 5(c). From Figs. 4 and 5, we observed that the main element in the surrounding of the groove fabricated in water was silicon, while that in ambient air were silicon and oxygen. No matter the silicon wafers were irradiated in water or ambient air, the whole cross section of the irradiated silicon wafer was polished by the abrasive paper; if the SiO_2 micro-grains in it contaminated the surface, oxygen should also be observed in the unirradiated regions in the same cross section; however, we did not observe oxygen in the cross section besides the irradiated regions, which confirmed that the SiO_2 micro-grain in the abrasive paper did not contaminate the measured regions. Therefore, we proposed that the incorporation of oxygen into the fabricated grooves could be effectively eliminated in water environment. As for the incorporation of oxygen into the interior of silicon, we contribute this phenomenon to the trapping effect of the laser induced dangling bonds.[26–28] When the femtosecond laser pulses irradiated the silicon wafer, there would be some defects formed in silicon, and some crystalline silicon transformed to amorphous silicon, the dangling bonds in which would trap the oxygen in ambient environment into silicon. Additionally, the dissolved oxygen in de-ionized water was much less than that in ambient air, the oxygen incorporated into the silicon immersed in water was so little that we could not observe it, on the contrary, the oxygen incorporated into silicon in ambient air cannot be ignored, and the atomic percentage of which was illustrated in Fig. 5.

We can see from Figs. 5(b) and 5(c) that the atomic percentage of oxygen decreases from the edge of the groove to the periphery regions in the transverse direction, and in the longitudinal direction, the atomic percentage of oxygen decreases with the increase of the depth. We attribute this phenomenon to the dependence of the incorporation of oxygen on the laser intensity. As the number of the induced dangling bonds is proportional to the intensity of the laser transmits inside the silicon material,[26] the amount of the photoinduced dangling bonds decreases from the center to the periphery regions due to the distribution of the incident laser in transverse direction; therefore, the atomic percentage of oxygen trapped into silicon decreases from the center to the periphery regions accordingly. In the longitudinal direction, intensity of the laser decreases along the propagation direction owing to the absorption of the laser in silicon material. For this reason, the induced dangling bonds decreases with the increase of the depth, the atomic percentage of oxygen trapped into silicon decreases accordingly, which shows the same dependence on the laser intensity as that in transverse

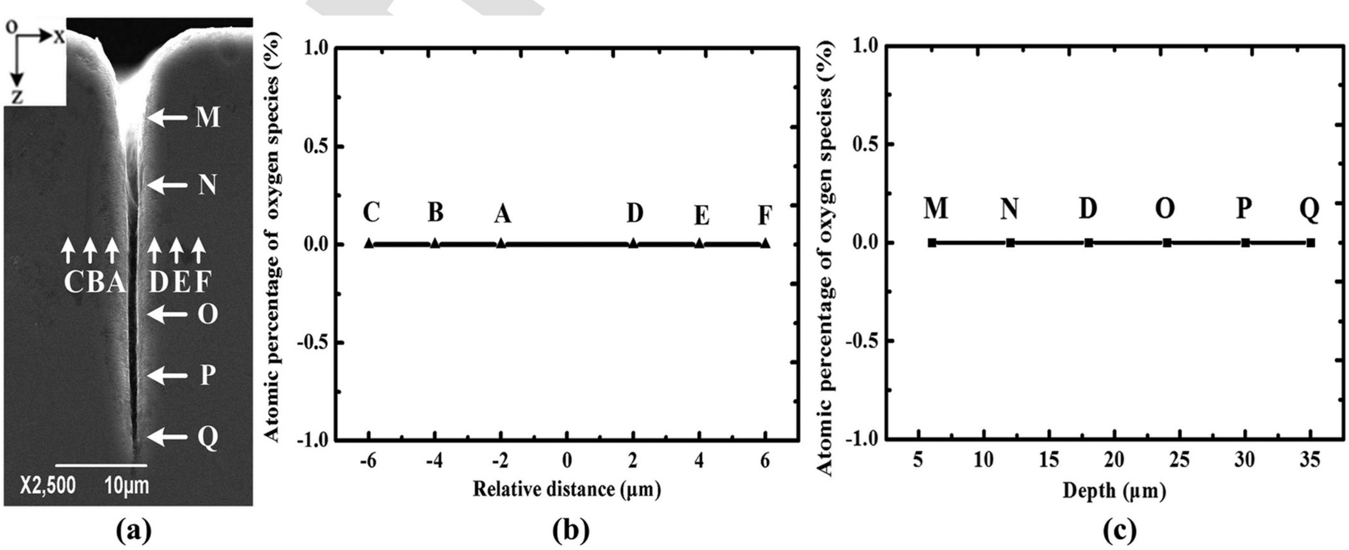

FIG. 4. Atomic percentage of oxygen species in the surrounding of the grooves fabricated in water: the measured points are marked out in (a), the atomic percentage of oxygen along the transverse and longitudinal directions are illustrated in (b) and (c), respectively.

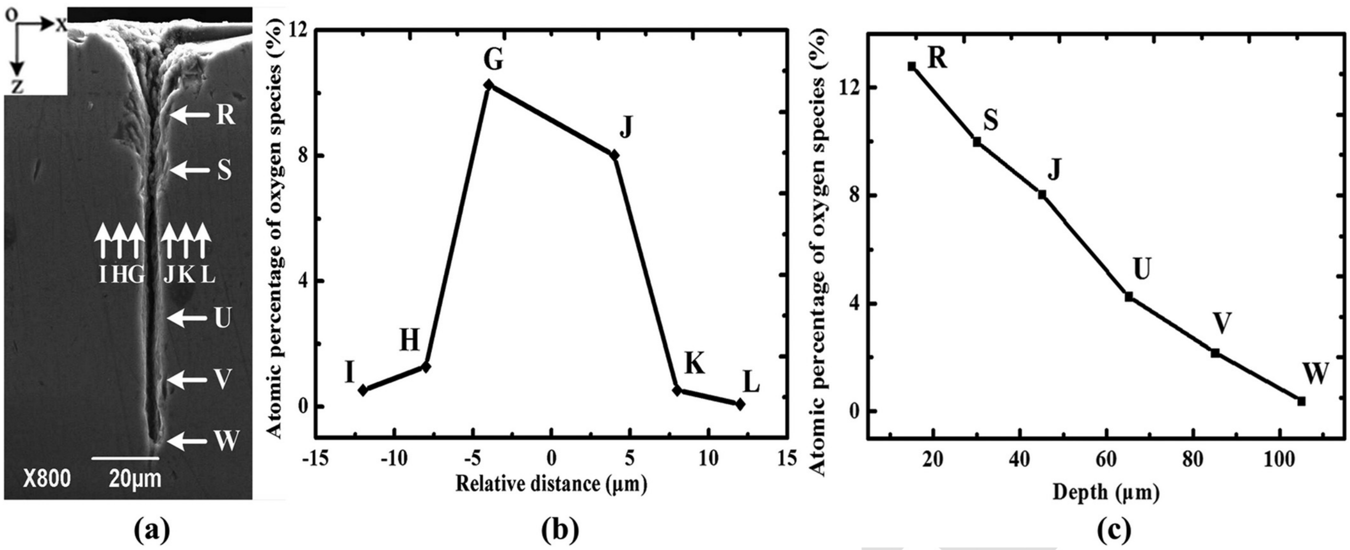

FIG. 5. Atomic percentage of oxygen species in the surrounding of the grooves fabricated in ambient air: the measured points are marked out in (a), the atomic percentage of oxygen along the transverse and longitudinal directions are illustrated in (b) and (c), respectively.

direction. What is more, the diffused oxygen decreases with the increase of depth may also lead to similar decrease of atomic oxygen percentage with increasing the depth in the longitudinal direction.

IV. CONCLUSIONS

In conclusion, we produced high-aspect-ratio grooves in de-ionized water and ambient air by a single pass of the tightly focused femtosecond laser pulses The sidewall of the grooves fabricated in de-ionized water was much smoother than those in ambient air, and there were nano-scale homogenous protrusions structures on the sidewall of grooves in de-ionized water. By comparing the chemical composition of these two kinds of grooves, we proposed that the incorporation of oxygen could be effectively eliminated in the de-ionized water environment, and the oxygen incorporation to the silicon wafer depends on the intensity of incident the laser.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support for this work provided by the National Science Foundation of China under the Grant No. 91123028, the National Basic Research Program of China (973 Program) under the Grant No. 2012CB921804, and the National Science Foundation of China under the Grant No. 11074197.

[1]S. K. Sundaram and E. Mazur, Nature Mater. **1**, 217–224 (2002).
[2]S. Kanehira, J. Si, J. Qiu, K. Fujita, and K. Hirao, Nano Lett. **5**, 8 (2005).
[3]K. C. Vishnubhatla, J. Clark, G. Lanzani, R. Ramponi, R. Osellame, and T. Virgili, Appl. Phys. Lett. **94**, 041123 (2009).
[4]G. A. Torchia, P. F. Meilan, A. Rodenas, D. Jaque, C. Mendez, and L. Roso, Opt. Express **15**, 20 (2007).
[5]Z. Chen and S. S. Mao, Appl. Phys. Lett. **93**, 051506 (2008).
[6]S. Lee, D. Yang, and S. Nikumb, Appl. Surf. Sci. **254**, 2996–3005 (2008).
[7]A. Borowiec, M. Mackenzie, G. C. Weatherly, and H. K. Haugen, Appl. Phys. A **76**, 201–207 (2003).
[8]C. Wang, H. Huo, M. Johnson, M. Shen, and E. Mazur, Nanotechnology **21**, 075304 (2010).
[9]~~R. Harzic,~~ H. Schuck, D. Sauer, T. Anhut, I. Riemann, and K. Konig, Opt. Express **13**, 17 (2005). AQ3
[10]B. Tan and K. Venkatakrishnan, J. Micromech. Microeng. **16**, 1–6 (2006).
[11]M. A. Sheehy, L. Winston, J. E. Carey, C. M. Friend, and E. Mazur, Chem. Mater. **17**, 3582–3586 (2005).
[12]R. Younkin, J. E. Carey, E. Mazur, J. A. Levinson, and C. M. Friend, J. Appl. Phys. **93**, 5 (2003).
[13]M. Y. Shen, C. H. Crouch, J. E. Carey, and E. Mazur, Appl. Phys. Lett. **85**, 23 (2004).
[14]S. Manickam, K. Venkatakrishnan, B. Tan, and V. Venkataramanan, Opt. Express **17**, 16 (~~2008~~).
[15]T. Chen, J. Si, X. Hou, S. Kanehira, K. Miura, and K. Hirao, Appl. Phys. Lett. **93**, 051112 (2008).
[16]C. Li, X. Shi, J. Si, F. Chen, T. Chen, Y. Zhang, and X. Hou, Appl. Phys. B **98**, 377–381 (2010).
[17]Y. Ma, H. Shi, J. Si, T. Chen, F. Yan, F. Chen, and X. Hou, Opt. Commun. **285**, 140–142 (2012).
[18]E. Hendry, F. J. Garcia-Vidal, L. Martin-Moreno, J. G. Rivas, M. Bonn, A. P. Hibbins, and M. J. Lockyear, Phys. Rev. Lett. **100**, 123901 (2008).
[19]G. V. Treyz, R. Beach, and R. M. Osgood, Appl. Phys. Lett. **50**, 8 (1987).
[20]G. V. Treyz, R. Beach, and R. M. Osgood, J. Vac. Sci. Technol. B **6**, 1 (1988).
[21]M. Mullenborn, H. Dirac, and J. W. Petersen, Appl. Phys. Lett. **66**, 22 (1995).
[22]T. H. R. Crawford, A. Borowiec, and H. K. Haugen, Appl. Phys. A **80**, 1717–1724 (2005).
[23]K. Venkatakrishnan, N. Sudani, and B. Tan, J. Micromech. Microeng. **18**, 075032 (2008).
[24]S. R. Aglyamov, A. B. Karpiouk, F. Bourgeois, A. Ben-Yakar, and S. Y. Emelianov, Opt. Lett. **33**, 12 (2008).
[25]A. B. Karpiouk, S. R. Aglyamov, F. Bourgeois, A. Ben-Yakar, and S. Y. Emelianov, J. Biomed. Opt. **13**, 034011 (2008).
[26]T. Kudrius, G. Slekys, and S. Juodkazis, J. Phys. D: Appl. Phys. **43**, 145501 (2010).
[27]Y. Izawa, Y. Izawa, Y. Setsuhara, M. Hashida, M. Fujita, R. Sasaki, H. Nagai, and M. Yoshida, Appl. Phys. Lett. **90**, 044107 (2007).
[28]T. H. R. Crawford, J. Yamanaka, G. A. Botton, and H. K. Haugen, J. Appl. Phys. **103**, 053104 (2008).