Applied Surface Science 289 (2014) 529–532

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Fabrication of through holes in silicon carbide using femtosecond laser irradiation and acid etching

Vanthanh Khuat[a,b], Yuncan Ma[a], Jinhai Si[a,*], Tao Chen[a], Feng Chen[a], Xun Hou[a]

[a] Key Laboratory for Physical Electronics and Devices of the Ministry of Education & Shaanxi Key Lab of Information Photonic Technique, School of Electronics & information Engineering, Xi'an Jiaotong University, No. 28, Xianning West Road, Xi'an 710049, China
[b] Le Quy Don Technical University, No. 100, Hoang Quoc Viet Street, Hanoi 7EN-248, Vietnam

ARTICLE INFO

Article history:
Received 18 September 2013
Received in revised form 5 November 2013
Accepted 7 November 2013
Available online 17 November 2013

Keywords:
Through holes
Laser affected zones
Chemical selective etching
Femtosecond laser
6H–SiC

ABSTRACT

By using 800-nm femtosecond laser irradiation and chemical selective etching, through holes were fabricated in a 350-μm silicon carbide sample. The morphology and chemical compositions of the through holes were characterized using scanning electronic microscopy equipped with an energy dispersive X-ray spectroscopy. The formation mechanism of the holes was attributed to the chemical reactions of laser affected zones with mixed solution of hydrofluoric acid and nitric acid. Results showed that chemical compositions of the area around the holes were silicon and carbon which were the same as those of the original one. Furthermore, the influences of number of pulses and pulse energy on the depth and diameter of the holes were investigated.

1. Introduction

Because of its small size, excellent performance, low cost and high volume production, microelectromechanical system (MEMS) has attracted increasing attention of researchers. Silicon-based MEMS devices have been well developed. These devices are generally limited in electronic devices performance to below 250 °C, and in mechanical device performance to below 600 °C [1]. They are not suitable working in corrosive environment since Si could be easily etched by acid solutions. Silicon carbide (SiC) is a promising candidate for MEMS applications [2–6] because of its outstanding physical and chemical properties. SiC-based devices are capable of working in harsh temperatures, wear, chemical, and radiated environment [7–11]. Therefore, SiC has been used in temperature sensors, gas sensors, pressure sensors, micromotors and resonators [12,13]. Unfortunately, because of its superior properties, SiC is difficult to etch; and there are no known wet enchants that could be used for bulk micromachining of SiC [14,15].

Commonly, the two main methods used for drilling and patterning SiC are photoelectrochemical (PEC) [2] and reactive ion etching (RIE) [16]. However, low processing rate, necessity of having micro-masks in etch field [14,17], and complexity of processing procedure are the main drawbacks of these methods.

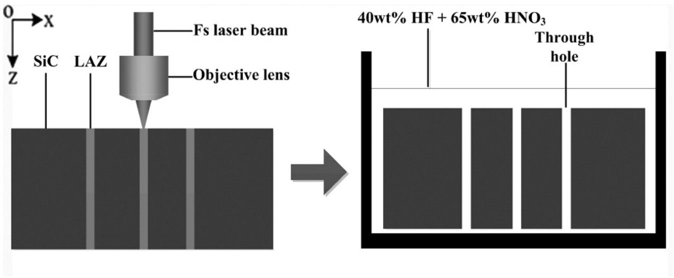
Recently, femtosecond laser has been proposed as an effective tool for micromachining SiC. Laser micromachining has several prominent advantages over the conventional methods, such as: noncontact processing, fast removal rates and being independent of etch masks [18,19]. Additionally, laser direct writing is capable of fabricating three dimensional micromechanical devices since the samples can be mounted onto a programmable positioning stage.

However, femtosecond laser drilling hole in SiC suffers from several limitations. First, since these experiments were performed in ambient air, the chemical composition of the induced holes would not be pure silicon carbide anymore. This means that foreign species could be trapped into the sample during fabricating process. This has a bad effect in the integration of SiC-based chips with other devices. Second, during laser treatment process, the light is scattered by the debris re-deposited around micro-voids, reducing the laser energy on incident spots, decreasing the depth of the holes. Finally, diameter of the hole decreases with the increase of the depth due to strong absorption near the surface of the pattern, reducing the aspect ratio of the hole. Because SiC is transparent to 800-nm light wave, 800-nm femtosecond laser is capable of inducing structural changes with high aspect ratio, which could be removed with proper etching technique. Therefore, we predict that the combination of 800-nm femtosecond laser with chemical etching could be ideal for fabricating through holes in SiC. However,

---

* Corresponding author. Tel.: +86 29 82663485.
E-mail address: jinhaisi@mail.xjtu.edu.cn (J. Si).

0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.11.030



(a) Laser irradiation **(b) Chemical selective etching**

Fig. 1. The schematic diagram of fabricating through hole in SiC; (a) experiment setup for laser irradiation; (b) experiment setup for chemical etching.

there has been no report about using this method to fabricate through holes in SiC.

In this work, we propose a simple method of fabricating through holes in 6H–SiC, in which femtosecond laser irradiation and chemical selective etching with mixed solution of hydrofluoric (HF) acid and nitric acid (HNO_3) were combined. First, laser affected zones (LAZ) were produced with the irradiation of 800-nm femtosecond laser. Then, mixed solution of HF and HNO_3 was used to remove the LAZ, forming the holes in SiC. Subsequently, SEM equipped with EDS was employed to characterize the morphology and chemical compositions of the LAZ and SiC through holes, respectively. Furthermore, we investigated the influences of number of pulses and pulse energy on the depth and diameter of the holes.

2. Experimental details

The schematic diagram of fabricating SiC with femtosecond laser is shown in Fig. 1. Fig. 1(a) shows the experimental setup for fabricating of LAZ in SiC. It contains: a femtosecond laser source, an attenuator, a neutral density filter, a mechanical shutter, a *xyz* movable stage, a computer and a CCD camera. The laser was an amplified Ti: sapphire femtosecond laser system (FEMTOPOWER Compact Pro, Austria) with pulse duration of 150 fs, wavelength of 800 nm, and repetition rate of 1 kHz. Attenuator provided a convenient way to adjust the laser energy, while mechanical shutter was employed to control the access of laser source. Movable stage, on which the SiC pattern could be mounted, controlled by computer program, allows us to fabricate on the pattern with high precision. The CCD camera was connected to computer for clear online observation in SiC pattern surface during fabricating process. The 10× microscope objective with NA of 0.3 was employed to focus laser onto the surface of 6H–SiC. The diameter of focal spot size of the NA is about 3.2 μm. The polarization direction of the incident laser is parallel to *y*-axis. Fig. 1(b) illustrates the etching experimental setup. Ultrasonic machine was used to accelerate etching process.

In ours experiments, the 6H–SiC pattern with thickness of 350 μm was used. Firstly, it was cleaned in acetone and de-ionized water with ultrasonic field for 10 min, respectively; then it was mounted on the movable stage. The laser beam was focused onto the pattern through an optical microscope objective lens. During fabrication surface of the pattern could be seen either through optical microscope or on the computer screen connected to CCD camera.

After laser irradiation, the pattern was cleaned consecutively with acetone and de-ionized water for 10 min before being selectively etched with mixed solution of 40 wt% HF and 60 wt% HNO_3 for 10 min. SEM equipped with EDS was employed to study the morphology and chemical compositions of the holes before and after being etched.

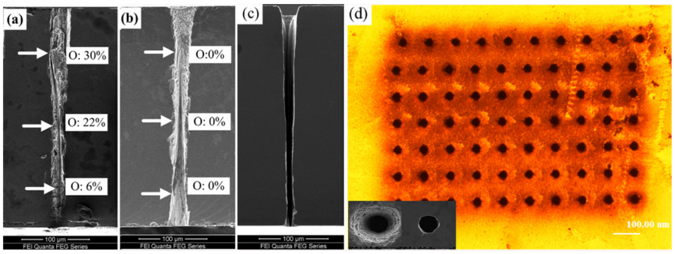


Fig. 2. Morphology of SiC through hole; (a) the LAZ, and the insets show atomic percentage of oxygen; (b) after etching and the insets show atomic percentage of oxygen; (c) cross section of micro groove after etching; (d) through holes array and the insets show the entrance and the end part of the hole, respectively.

3. Results and discussion

Fig. 2 shows the morphology and chemical composition of the LAZ and the chemical etching induced SiC through holes. The holes were fabricated in ambient air. The pulse energy and number of pulses were 40 μJ and 3000, respectively. After being irradiated with 800-nm femtosecond laser, the LAZ was induced at the irradiated zones in the direction of the laser transmission as shown in Fig. 2(a). It is worth mentioning that the theoretical Rayleigh length of the NA is 2.8 μm; while the length of LAZ is 350 μm. This is because of the occurring of the self-focusing induced by high laser fluence that leads to long lasting filament which travel over the thickness of the pattern. The insets show the atomic percentage of oxygen (O) at the points marked with the arrows. The formation of LAZ is attributed to the diffusion of O into SiC caused by the interaction of femtosecond laser and the material. For ultrashort laser pulse, multiphoton absorption is considerably strong. Although 800-nm photons cannot meet 6H–SiC band gap energy (3.1 eV) requirements, bond breaking is induced by multiphoton absorption associated with extreme intensity. As a result dangling bond, which is capable of trapping in O atomic, could be generated. And the incorporation of O in the material could be attributed to the trapping effect of dangling bond [20]. EDS results, as shown in the insets, show the evidence of the presence of O in the interior of the SiC substrate along the transmission direction.

After the laser treatment, the pattern was etched with mixed solution HF and HNO_3 for 10 min. Due to the chemical reactions of mixed solution HF and HNO_3 with LAZ, according to the above analysis, possibly composed of: SiO_2, Si and amorphous SiC, the LAZ was completely removed, forming the hole in SiC as shown in Fig. 2(b). The following formulas are the related chemical processes [21,22].

$$Si(s) + 4HNO_3(aq) \rightarrow SiO_2(s) + 2H_2O(aq) + 4NO_2(g) \quad (1)$$

$$\begin{aligned} &SiC(amorphous) + 2HNO_3(aq) + 2H_2O \\ &\quad \rightarrow 2HNO_2(aq) + SiO_2(s) + CO_2(g) + 2H_2(g) \end{aligned} \quad (2)$$

$$SiO_2(s) + 6HF(aq) \rightarrow H_2SiF_6(aq) + 2H_2O(aq) \quad (3)$$

In the above reaction progress, HNO_3 acts as the oxidizing agent, and HF removes the silicon oxide generated from the laser ablation process, reactions (1) and (2). It should be noticed that only the LAZ reacted with acid solution, but the surrounding zones remained unchanged. This indicates the high selectivity of the method. After being etched, the wafers were rinsed in ultrasonic cleaner with acetone and de-ionized water for 10 min to eliminate the remained reactants HF and HNO_3 and by-product fluosilicic acid (H_2SiF_6), respectively. It should be noticed that atomic percentages of O in surrounding area of the holes were in the range of the measurement deviation of EDS analysis and could be ignored. Because the

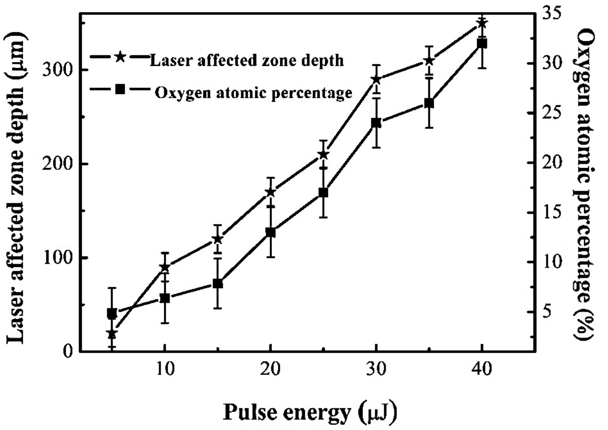


Fig. 3. Depth and oxygen concentration of the LAZ versus pulse energy.

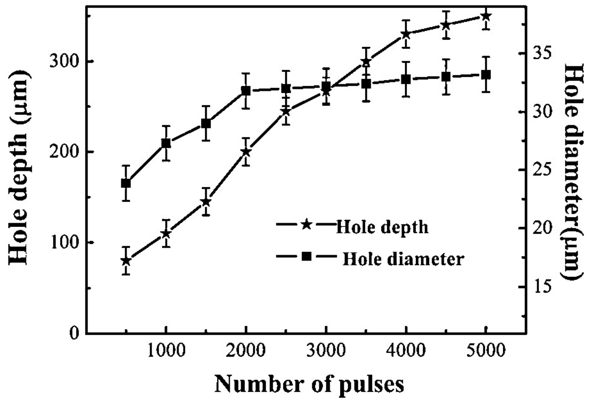


Fig. 4. Depth and diameter of the holes versus number of pulses.

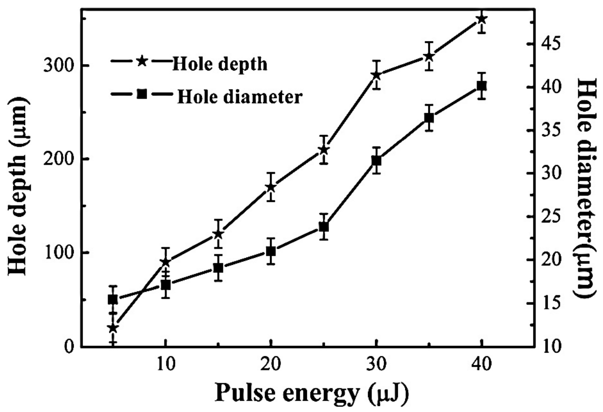


Fig. 5. Depth and diameter of the holes versus pulse energy.

side wall of the hole is usually greatly damaged after being polished, it is very difficult to obtain to the surface roughness of the hole. For this reason the side wall of the micro-groove fabricated with the same laser parameters was used to analyze the surface roughness of the hole. Fig. 2(c) shows the cross-section of micro groove. It can be seen that the side wall is quite smooth. The surface roughness is smaller than 0.5. In addition, as can be seen in Fig. 2 (d) and the insets, the holes are almost circular in shape.

Fig. 3 shows the dependence of the concentration of O in LAZ on pulse energy. The pulse energy was varied from 5 μJ to 40 μJ with increment of 5 μJ. The number of pulses was set to be 3000. In order to investigate the influence of pulse energy on O concentration, for each LAZ, the O atomic percentage at point of 60 μm below the surface was used. It is obvious that concentration of O increases with the increase of pulse energy. This is because the concentration of femtosecond laser induced dangling bonds increases with the increase of pulse energy. Therefore, the ability of SiC to accommodate foreign species of O increases, resulting in the increase of the atomic percentage of O species in LAZ.

We also investigated the influence of number of pulses on the depth and diameter of the hole. Pulse energy was 30 μJ; while number of pulses was set from 500 to 5000 with increment of 500. Fig. 4 demonstrates the dependence of depth and diameter of the hole on the number of pulses. It is obvious that the depth increases as number of pulses increases. As mentioned above, multiphoton absorption associated with extreme intensity of femtosecond pulse is responsible for bond breaking and subsequent creation of dangling bond in SiC. As the number of pulses increases, more laser energy could be absorbed by the material, resulting in the increase of the LAZ depth. Furthermore, because the concentration of the femtosecond laser induced dangling bond increases with the increases of number of pulses, more foreign species of O would be trapped into the SiC substrate. As a result, chemical and physical properties of the LAZ are less stable as compared to those of the original one; this could accelerate the etching process. Therefore, the depth of LAZ and depth of the SiC holes increases with the increase of number of pulses. Meanwhile, when number of pulses increases, the diameter slightly increases at first and almost keep unchanged as number of pulses reaches 2000. This is because the effective area on the material mainly depends on the pulse energy. As the pulse energy keeps unchanged, the effective area rapidly reaches its peak and almost makes no significant change regardless of the number of pulse.

Fig. 5 demonstrates the dependence of the depth and diameter of the holes on E. Number of pulses was set at 3000; while pulse energy was set from 5 μJ to 40 μJ with increment of 5 uJ. It is obvious that the depth and diameter of the hole increase as E increases. Since multiphoton absorption associated with extreme intensity of femtosecond pulse is responsible for bond breaking and subsequent creation of dangling bond in SiC. The higher the pulse energy, the deeper the LAZ is generated. This leads to the increase of the depth of the hole. Meanwhile, the higher pulse energy, the larger the effective irradiation areas on the SiC surface. Therefore, the depth and diameter of the holes increase with the increase of pulse energy.

Additionally, in the etching process, as the etching time increases the diameter rapidly reaches a certain value then it keeps unchanged. This is because the mixed solution is effective to LAZ only. This demonstrates the high selectivity of the method.

4. Conclusions

In conclusion, we proposed a simple method of fabricating through holes in 6H–SiC using femtosecond laser and chemical selective etching. First, LAZ were induced on the SiC pattern. Then the holes were produced as the LAZ were removed by chemical selective etching with mixed solution of HF and HNO_3. The formation mechanism of the SiC holes was attributed to the chemical reaction of the LAZ with mixed solution of HF and HNO_3. By using SEM equipped with EDS, the morphology and chemical composition of the holes were characterized. Furthermore, the effects of pulse energy and number of pulses on the depth and diameter of the holes were systematically investigated.

Compared with traditional ones, the method has several prominent advantages, such as: fast removal rate, being independent of etch mask, being simple technological process and high precision and flexibility of controlling the depth of the hole. It is expected that the method could be potentially used in many applications of fabricating of SiC-based advanced functional materials.

Acknowledgements

The authors gratefully acknowledge the financial support for this work provided by the National Natural Science Foundation of China (NSFC) under the Grant Nos. 91123028 and 61235003, and the National Basic Research Program of China (973 Program) under Grant No. 2012CB921804. The authors also sincerely thank Ms. Dai at International Center for Dielectric Research (ICDR) in Xi'an Jiaotong University for the support of SEM and EDS measurements.

References

[1] M. Mehregany, C.A. Zorman, N. Rajan, C.H. Wu, Proc. IEEE 86 (1998) 1594–1609.
[2] L. Jiang, R. Cheung, M. Hassan, A.J. Harris, J.S. Burdess, C.A. Zorman, M. Mehregany, J. Vac. Sci. Technol. B 21 (2003) 2998–3001.
[3] I.A. Salama, N.R. Quick, A. Kar, J. Electron. Mater. 31 (2002) 200–208.
[4] Z. Tian, N.R. Quick, A. Kar, Acta Mater. 54 (2006) 4273–4283.
[5] A. Ikeda, K. Nishi, H. Ikenoue, T. Asano, Appl. Phys. Lett. 102 (2013) 052104.
[6] P. Rudolph, K. Brzezinka, R. Wäsche, W. Kautek, Appl. Surf. Sci. 208 (2003) 285–291.
[7] I. Shigematsu, K. Kanayama, A. Tsuge, M. Nakamura, J. Mater. Sci. Lett. 17 (1998) 737–739.
[8] H. Morkoc, S. Strite, G.B. Gao, M.E. Lin, B. Sverdlov, M. Burns, J. Appl. Phys. 76 (1994) 1363–1398.
[9] K. Yamamura, T. Takiguchi, M. Ueda, H. Deng, A.N. Hattori, N. Zettsu, Cirp. Ann-manuf. Techn. 60 (2011) 571–574.
[10] B. Pecholt, S. Gupta, P. Molian, J. Laser Appl. 23 (2011) 012008.
[11] P.M. Sarro, Sens. Actuators, A 82 (2000) 210–218.
[12] Y. Dong, C. Zorman, P. Molian, J. Micromech. Microeng. 13 (2003) 680.
[13] D. Gao, M.B. Wijesundara, C. Carraro, R.T. Howe, R. Maboudian, Sens. J. IEEE 4 (2004) 441–448.
[14] M. Farsari, G. Filippidis, S. Zoppel, G.A. Reider, C. Fotakis, J. Micromech. Microeng. 15 (2005) 1786.
[15] S. Zoppel, M. Farsari, R. Merz, J. Zehetner, G. Stangl, G.A. Reider, C. Fotakis, Microelectron. Eng. 83 (2006) 1400–1402.
[16] A. Szczęsny, P. Śniecikowski, J. Szmidt, A. Werbowy, Vacuum 70 (2003) 249–254.
[17] C. Li, X. Shi, J. Si, T. Chen, F. Chen, S. Liang, Z. Wu, X. Hou, Opt. Commun. 282 (2009) 78–80.
[18] A.N. Samant, N.B. Dahotre, J. Eur. Ceram. Soc. 29 (2009) 969–993.
[19] H.W. Choi, Thesis, Ohio State University, Ohio, 2007.
[20] Y. Ma, H. Ren, J. Si, X. Sun, H. Shi, T. Chen, F. Chen, X. Hou, Appl. Surf. Sci. 261 (2012) 722–726.
[21] M. Steinert, J. Acker, S. Oswald, K. Wetzig, J. Phys. Chem. C 111 (2007) 2133–2140.
[22] J. Zhu, Z. Liu, X.L. Wu, L.L. Xu, W.C. Zhang, P.K. Chu, Nanotechnology 18 (2007) 365603.