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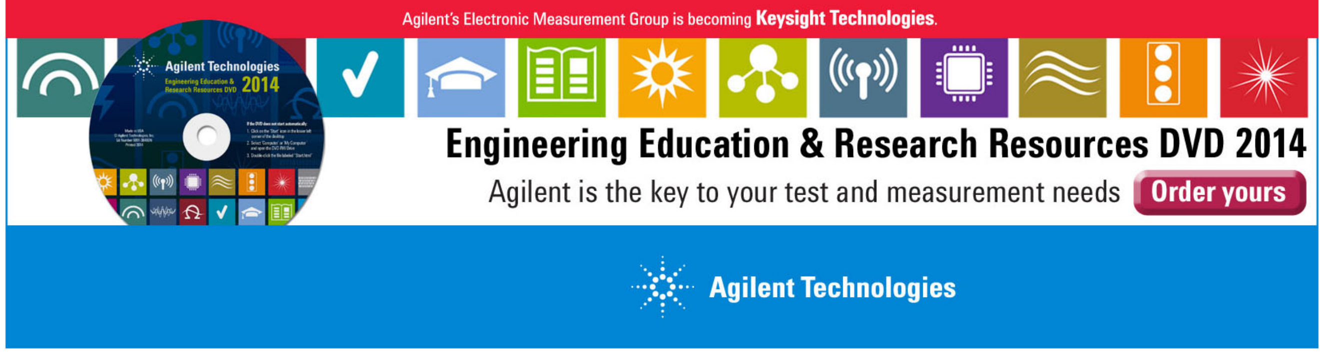

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Uniform nano-ripples on the sidewall of silicon carbide micro-hole fabricated by femtosecond laser irradiation and acid etching

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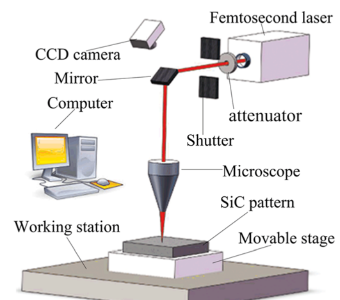
Uniform nano-ripples were observed on the sidewall of micro-holes in silicon carbide fabricated by 800-nm femtosecond laser and chemical selective etching. The morphology of the ripple was analyzed using scanning electronic microscopy. The formation mechanism of the micro-holes was attributed to the chemical reaction of the laser affected zone with mixed solution of hydrofluoric acid and nitric acid. The formation of nano-ripples on the sidewall of the holes could be attributed to the standing wave generated in *z* direction due to the interference between the incident wave and the reflected wave. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4883880]

Due to its ability to deposit energy into a transparent material through high-order nonlinear absorption, femtosecond laser has been proved to be a versatile micromachining tool with submicrometer precision.[1–6] Specifically, it has been applied to drilling,[7–10] patterning,[11,12] and synthesizing[13] various types of microstructures and nanostructures in silicon carbide (SiC) which is known for its unique physical and chemical properties.[14–18] Among these structures, periodic nanostructures have gained considerable attention of researchers due to its potential applications in photovoltaic, surface texturing, and three-dimensional data storage. Accordingly, there have been many studies on the fabrication and the formation mechanism of periodic nanostructures on SiC.[13,19–21] However, most of the work mainly focused on the fabrication of nanostructures on the surface of the pattern.

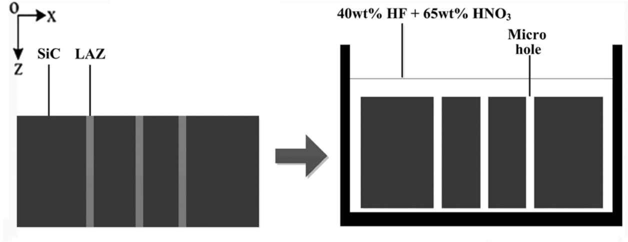
The incorporation of nanostructures inside micro-holes can diversify its function.[22] For example, in the droplet-based microfluidic application, the nanostructures inside microfluidic channels can dramatically reduce the flow resistance.[23] Nanostructure in microfluidic chip was used to trap different types of dielectric structures, including living cells.[24] In addition, nano-Bragg grating device integrated with microfluidic channels has been used for bio-sensing applications.[25] Recently, Ahsan[26] reported on the formation of nanostructures in micro-holes in soda–lime, however, in which the nanostructure is not uniform, and the chemical composition of the nanostructure has not been investigated. SiC has been recognized as an excellent candidate for bio-sensor application in which the incorporation of the foreign species such as oxygen (O) should be avoided.

In this Letter, we report on the formation of uniform nano-ripples on the sidewall of the SiC micro-holes fabricated by the femtosecond laser irradiation and chemical selective etching with mixed solution of hydrofluoric acid (HF) and nitric acid (HNO_3). First, the laser affected zone (LAZ) was produced with the irradiation of an 800-nm femtosecond laser. Then, mixed solution of HF and HNO_3 was used to remove the LAZ, forming micro-holes in SiC. Subsequently, scanning electronic microscopy (SEM) equipped with an energy dispersive X-ray spectroscopy (EDS) was employed to characterize the morphology and chemical composition of the holes before and after being etched, respectively.

The schematic diagram of fabricating SiC with femtosecond laser and chemical selective etching is shown in Figure 1. Figure 1(a) shows the experimental setup for fabricating 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 charge coupled device (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



(a) Laser irradiation



(b) Chemical selective etching

FIG. 1. The schematic diagram of fabricating micro holes in SiC: (a) Experiment setup for laser irradiation; (b) Experiment setup for chemical etching.

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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 the 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 the fabricating process. The microscope objective lens was employed to focus laser onto the pattern. Figure 1(b) illustrates the etching experimental setup. Ultrasonic cleaner was used to accelerate the etching process.

In our experiments, the 6H silicon carbide (6H-SiC) pattern with thickness of 350 μm was used. First, 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 surface of the pattern by a 10× microscope objective lens with numerical aperture (NA) of 0.3. The micro-holes were fabricated in ambient air. The laser pulse energy and pulse number were set at 35 μJ and 10 000, respectively. During the fabrication, the surface of SiC pattern could be seen either via optical microscope or on the computer screen connected to CCD camera. The laser was adjusted to be circularly polarized light.

After the laser irradiation, we polished the SiC pattern with water proof abrasive papers to observe the LAZ from the cross section. The pattern is then cleaned consecutively with acetone and de-ionized water for 10 min before being selectively etched with mixed solution of 40 wt. % HF and 65 wt. % HNO_3 (volume ratio 1:1) for 10 min. We polished the pattern to see the sidewall of the hole again. SEM equipped with an EDS was employed to study the morphology and chemical composition of SiC hole and the sidewall before and after being etched.

Figures 2(a) and 2(b) show the morphology and chemical composition of the cross section of LAZ and the chemical etching induced SiC hole. After being irradiated with 800-nm femtosecond laser, the LAZ was induced at the irradiated zone in the direction of the femtosecond laser transmission as shown in Figure 2(a). The insets show the atomic percentage of O at the points marked with the arrows. The formation of LAZ is attributed to the dangling bonds generated in SiC crystal lattice by the femtosecond laser irradiation. For ultra-short 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 the high intensity of femtosecond pulses. As the result, dangling bonds appeared in the crystal lattice of SiC. These dangling bonds make the LAZ chemically and physically less stable as compared to the original SiC. And the incorporation of O in the material could be attributed to the trapping effect of dangling bond.[27] 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. The O atom probably existed in the LAZ in the form of silicon oxides (SiO_x). And the Si and non-stable form of SiC could also be generated during the laser irradiation as a result of the bond breaking. To sum up, the LAZ possibly composes of SiO_x, Si, and non-stable form of SiC.

After the laser treatment, the pattern was etched with mixed solution of HF and HNO_3 for 10 min. The LAZ reacted with the solution and was completely removed, forming the holes in SiC as shown in Figure 2(b). We interpreted the phenomenon as follows: SiO_x induced by the femtosecond laser in the LAZ was removed by the HF;[28] while the Si and SiC was first being oxidized by the HNO_3 to form silicon dioxide (SiO_2), which was further removed by the HF. Following are the related chemical processes:[29,30]

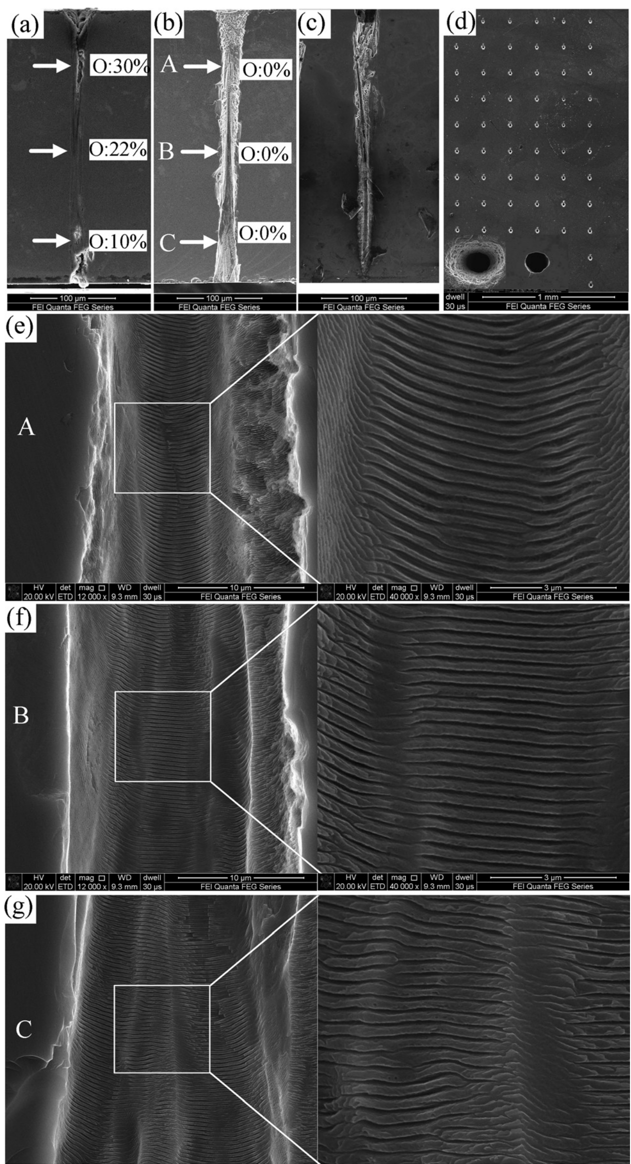

FIG. 2. SEM images morphology of SiC micro-hole and nano-ripples on the sidewall; (a) The LAZ, the insets show atomic percentage of O in the LAZ at the points marked with arrows; (b) After etching with mixed solution of HF acid and HNO_3 acid; (c) After etching with HNO_3 acid; (d) Micro-holes array, and the insets show magnified view of the entrance and the end part of a hole, respectively; (e)–(g) Magnified view of nano-ripples on the sidewall in the area marked with arrows in Fig. 2(b).

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

$$SiC(amorphous) + 2HNO_3(aq) + 2H_2O = 2HNO_2(aq) + SiO_2(s) + CO_2(g) + 2H_2(g), \quad (2)$$

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

In the above reaction progress, HNO_3 acts as the oxidizing agent, and HF removes the silicon oxides generated from

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the laser irradiation process and the chemical oxidizing process of Si and SiC by HNO_3 in reaction (1) and (2). It should be noticed that only the LAZ reacted with the acid solution and was removed, while the surrounding zone which was chemically more stable with the mixed solution than the LAZ was not removed. This indicates the high selectivity of the method. After the etching, the wafers were rinsed in the ultrasonic cleaner with acetone and de-ionized water for 10 min to eliminate the remained reactants HF and HNO_3 and the by-product fluosilicic acid (H_2SiF_6), respectively. The atomic percentages of O in surrounding area of the micro-holes were in the range of the measurement deviation of the EDS analysis and could be ignored. Figure 2(d) shows the micro-holes array fabricated by the method; the insets show magnified view of the entrance and the end part of the hole, respectively.

Figure 2(c) shows the LAZ after etched with HNO_3 (wt. % 65) acid solution for 30 min. It could be seen that HNO_3 could not remove the LAZ. We speculate that the HNO_3 could only oxidize the LAZ to form silicon oxides as shown in formula (2); the formation of silicon oxides, in turn, ceased the reaction of the LAZ and the acid, as the consequence the oxidizing process stopped.

Figures 2(e)–2(g) show the morphology of nano-ripples at different positions along z direction. It is obvious that clear nano-ripples were observed on entire of the sidewall of the hole. The periodicity of nano-ripples is about 310 nm. There has been no report concerning nano-ripples on sidewall of the micro-holes in SiC. The formation of nano-ripples on the sidewall of the holes could be attributed to the standing wave generated in z direction due to the interference between the incident wave and the reflected wave from the interface of LAZ and the pristine material which was perpendicular to z direction. It is worth mentioning that the position of the interface was changed with the laser irradiation time as the depth of the LAZ increased with the laser irradiation time. The formation of the standing wave led to the permanent structural changes in SiC, forming the pre-form of the nano-ripples. As the pattern was treated with proper etching technique, the LAZ was removed, resulting in the nano-ripples on the sidewalls of the holes. The distance between two conjugative nodes of the standing wave, which is equal to the periodicity of the nano-ripples, should be $\lambda/(2 \times n_{LAZ})$. λ is wavelength of incident wave, and n_{LAZ} is refractive index of the LAZ during the laser irradiation. The periodicity of the nano-ripples is about 310 nm, which implies that n_{LAZ} is about 1.3, which is much smaller than that of the original SiC. We reason that the small refractive index in the LAZ was due to the combined effect of laser-induced plasma and laser melting SiC. As well known, laser-induced lattice-defect in the LAZ increases with the increase of pulse energy and pulse number. As the results, grain boundaries could be formed and the temperature here rises. Melting at the grain boundaries may take place.[31] At this stage, the LAZ may exist in liquid state, and its refractive index could be as small as that of liquid. At the mean time, laser-induced high density plasma could also be formed as the result of bond-breaking process caused by multiphoton absorption.[32] The plasma could have negative contribution to the refractive index of the LAZ. The refractive index change caused by plasma is: $\Delta n = -\rho/2\rho_c$, where ρ is the density of free electron and ρ_c is the value of critical plasma density ($\rho_c = 1.75 \times 10^{21}\,\text{cm}^{-3}$ at 800 nm).[33,34] Assuming that the refractive index of the melting SiC is about 1.5, it can be calculated that the change in refractive index cause by plasma is 0.2. Then, the density plasma could be achieved $\rho = 0.7 \times 10^{21}\,\text{cm}^{-3}$. Meanwhile, the change in structure of the LAZ caused by laser irradiation could also contribute to the reduction of its refractive index.

In order to understand the influence of laser pulse energy on the nano-ripples on the sidewall of the hole, the pulse number was fixed to be 10 000, while different laser energy pulses were applied. Figure 3 shows the ripples with different laser pulse energy. It could be seen that periodicity of the ripples decreases with the decrease of the laser pulse energy; and the higher the laser pulse energy, the clearer the nano-ripples. This is due to the fact that melting effect and laser-induced plasma which could reduce the refractive index of LAZ are highly dependent on the laser power. As the laser pulse energy decreases, the number of the electrons excited

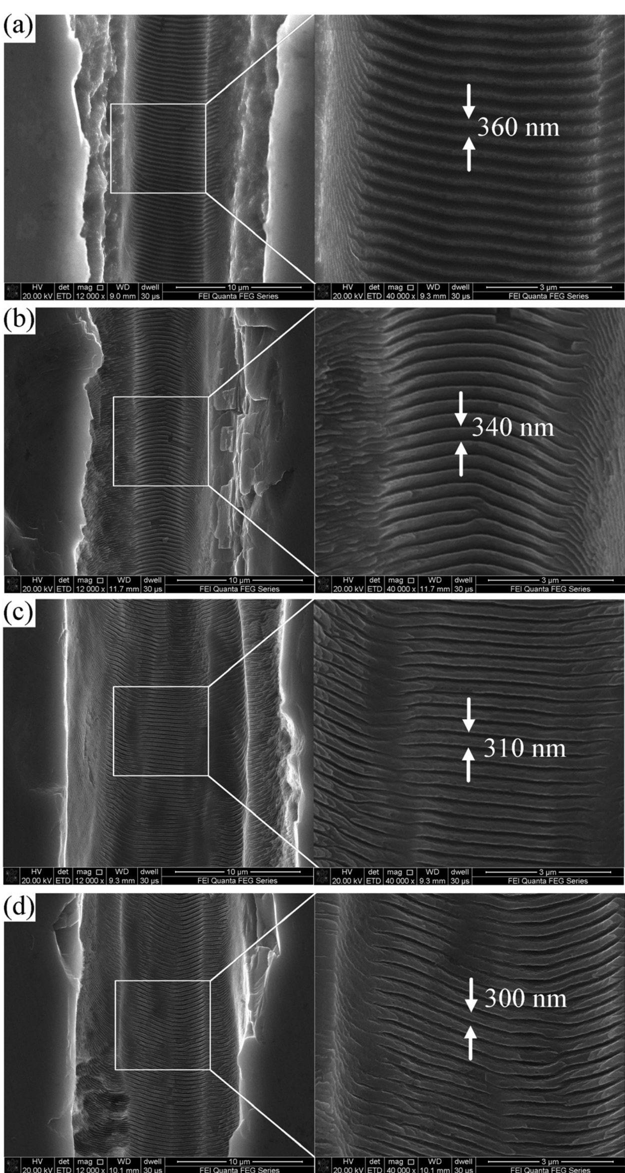

FIG. 3. Nano-ripples fabricated with different laser pulse energy; (a) 45 μJ; (b) 40 μJ; (c) 35 μJ; (d) 30 μJ.

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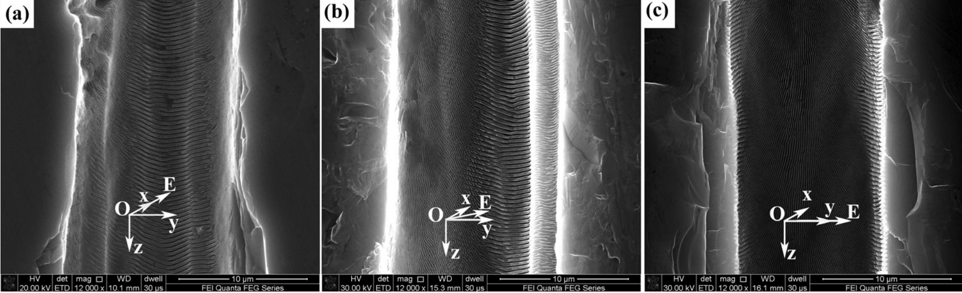

FIG. 4. Influence of polarization on nano-ripples; (a) **E** perpendicular to the surface; (b) The angle of **E** and the surface is 45°; (c) **E** is parallel to the surface.

from the valence band to the conduction band via multiphoton absorption and impact ionization decreases.[35] This means that the density of the free electrons in the conduction band decreases with the decrease of laser pulse energy. Therefore, n_{LAZ} increases with the decrease of laser pulse energy. As a result, periodicity of the nano-ripples decreases with the decrease of laser pulse energy. At the mean time, higher laser pulse energy could lead to higher intensity of antinode of the standing wave and pattern imprinted on the sidewall could be clearer after etching.

In order to understand the influence of the laser polarization on the nano-ripples, the laser was adjusted to be linearly polarized light, and the holes were fabricated at 0°, 45°, and 90° polarization angles. Figure 4 shows the influence of laser polarization to the ripples. As shown in Figure 4(a), the nano-ripples could be achieved with electric field (**E**) perpendicular to the hole-wall surface. However, as the polarization angle was changed, instead of the uniform ripples, nanostructure with periodicity of about 145 nm (fine ripple) was formed as shown in Figures 4(b) and 4(c). It could be seen that this kind of nano-structures is similar to that reported in Ref. 36, in which the polarization of the incident laser is parallel to the sample surface. We reason that there exists the competition between the many complex processes such as: interference of incident light and laser-excited field, and the formation of the standing wave. And each of them could give rise to the production of structures on the sidewall of the hole. In this case, it is hypothesized that for polarization parallel to the wall surface, the nano-ripples produced by the standing wave were replaced by the nano-structures produced by other processes which are not in the scope of this paper.

We fabricated uniform nano-ripples on the sidewall of micro-holes in silicon carbide fabricated by 800-nm femtosecond laser and chemical selective etching. The morphology of the ripples was analyzed by SEM equipped with an EDS. The formation mechanism of SiC micro-holes was attributed to the chemical reaction of the LAZ with mixed solution of HF and HNO_3. The formation of uniform nano-ripples in the sidewall of the holes could be attributed to the standing wave in z direction. The result showed that the nano-ripples distributed on entire the sidewall. The periodicity of nano-ripples decreases with the decrease of laser pulse energy. The nano-ripples were of good quality. It is expected that this technique could be applied in biosensor applications such as: Bio MEMS and microfluidic biosensor, and applications that requires certain adhesion properties and wettability of the surface of the micro-holes.

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