

Direct, parallel nanopatterning of silicon carbide by laser nanosphere lithography

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Abstract. A technique to create nanopatterns on hard-to-machine bulk silicon carbide (SiC) with a laser beam is presented. A monolayer of silica (SiO₂) spheres of 1.76- μ m and 640-nm diameter are deposited on the SiC substrate and then irradiated with an Nd:YAG laser of 355 and 532 nm. The principle of optical near-field enhancement between the spheres and substrate when irradiated by a laser beam is used for obtaining the nanofeatures. The features are then characterized using a scanning electron microscope and an atomic force microscope. The diameter of the features thus obtained is around 150 to 450 nm and the depths vary from 70 to 220 nm. © 2006 Society of Photo-Optical Instrumentation Engineers. [DOI: 10.1117/1.2177288]

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1 Introduction

Silicon carbide (SiC) has very high thermal conductivity, a high melting point, low thermal expansion coefficient, high breakdown electric field, and high electron saturation. SiC is a transparent material, and since it has high bandgap energy, the material is of great importance in electronic and optoelectronic applications. SiC-based devices are attractive for blue light-emitting diodes (LEDs), thyristors, U-shaped grooved MOS (UMOS) devices, and UV photodiodes.¹ SiC is used in devices that operate in harsh environments like the combustion chamber of an automobile engine, where it is incorporated into the membrane of the pressure sensor. Schottky-based diodes (SBDs) fabricated on 6H-SiC substrates showed high blockage voltages. SiC junction field effect transistors (JFETS) are used in developing a hybrid switch by combining it with a low-voltage silicon MOSFET, for use in resonant converters and auxiliary power supplies.² To fabricate any SiC-based devices with micropatterns, a dry etching technique was used, and the etching rate is low due to the strong binding energy of SiC.³ Also, there are no wet etchants that can bulk micromachine SiC, as it is chemically very stable and is actually nature's best etch-stopping material. SiC surface micromachining is also a very difficult task like SiC bulk micromachining. Therefore, a novel technique for micro-, even nanoscale, patterning of SiC is in urgent need.

Recently, a laser micromachining technique emerged as a simple, direct-write process for engineering materials.⁴ It is a simple and clean method, and very high etch rates can be achieved. Also, lasers are used in fabricating high-aspect-ratio holes with small diameters at designed locations for cutting and scribing applications. However, for breaking a bond in SiC, either a high energy density nanosecond (ns) laser or femtosecond (fs) laser is needed. Femtosecond lasers have been used for ablating 1- μ m-thick SiC (3C-SiC) films on silicon. At high laser fluence, the

process is thermally dominated by melting, boiling, and vaporizing the single crystal SiC, and at lower laser fluences, the ablation is a defect activated process.⁵ Femtosecond laser micromachining of SiC relies on multiphoton absorption.⁶ A ns copper vapor laser (510- and 572-nm wavelength) with energy density as high as 16 J/cm² has been used for etching polycrystalline SiC, and despite the high energy density employed, the etching rate was very low both in air and liquid (water, DMSO).⁷

Hybrid laser processing is also used for the microfabrication of hard and transparent materials like SiC, where a nanosecond pulsed laser beam is used with a medium on the transparent material surface. The medium is used for absorbing the laser beam and generating plasma that would assist in the high-quality ablation of transparent materials. This kind of process is called laser-induced plasma-assisted ablation (LIPAA).⁸ By the nonlinear interaction of a fs laser with transparent materials, microplasma could be generated within the material, which on subsequent expansion, results in the fabrication of a small structure. Also, by initiating a microexplosion inside the material, a small cavity can be formed with the material ejected from the center.⁹

As seen from the previously mentioned studies, the processes used for the microfabrication of SiC require very high energies with a complicated optical setup. Also, due to the diffraction limit of light, it is difficult to obtain nanometer-sized features. To overcome the previously mentioned difficulties, the enhancement of the optical near-field obtained by irradiating nanospheres by laser radiation can be used. This enhanced intensity distribution is very sensitive to the diameter of the spheres and to the distance between the sphere and the substrate.¹⁰ Mie-theory calculations have shown that the enhancement is mainly due to the near-field and scattering effects.¹¹ Using this enhanced near-field, silicon and borosilicate glass were massively patterned with a nanosecond (ns) pulsed laser.^{12,13}

In the present study, the parallel nanopatterning of bulk SiC is attempted by using a nanosecond pulsed laser, irradiating through a monolayer of silica nanospheres on SiC.

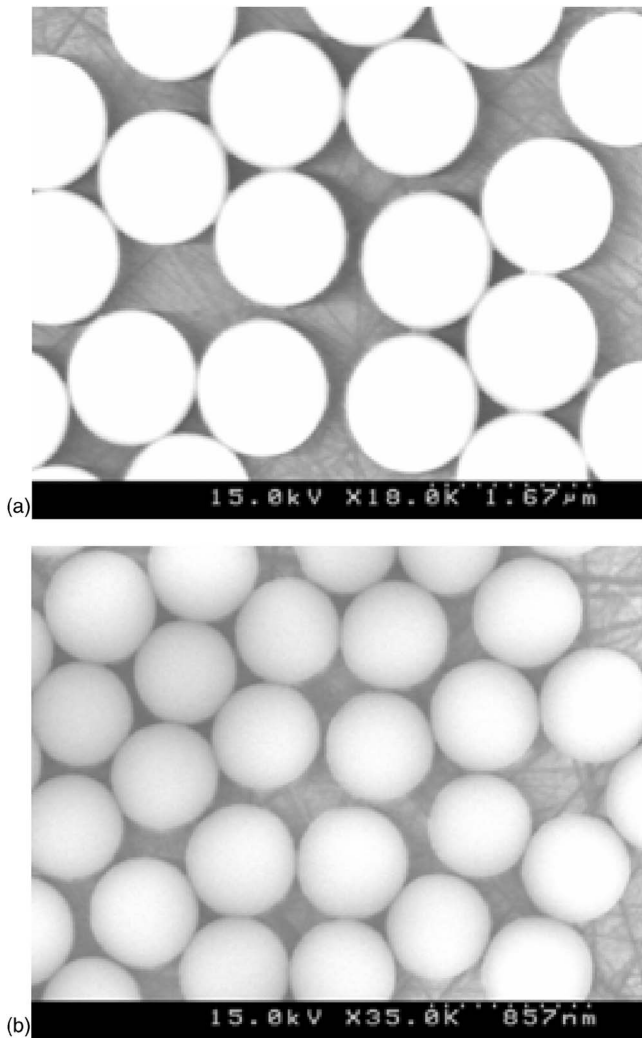


Fig. 1 SEM micrograph of the monolayer of silica spheres with a diameter of (a) $1.76 \mu\text{m}$ and (b) 640 nm .

An Nd:yttrium-aluminium-garnet laser (10-ns pulse duration) is used with two different wavelengths, 355 and 532 nm, to study the effect of different photon energies in creating nanofeatures. Different sphere diameters ($1.76 \mu\text{m}$ and 640 nm) are also used to understand its effect on the features obtained on the SiC substrate.

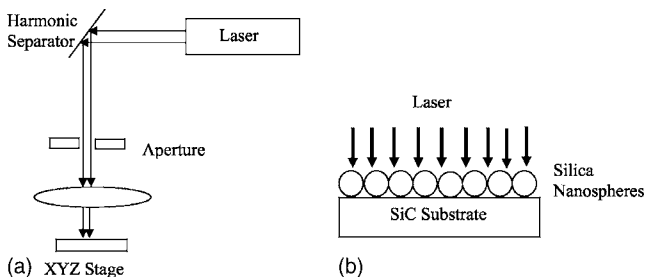


Fig. 2 Schematic of (a) experimental setup and (b) irradiation of the silica spheres on SiC.

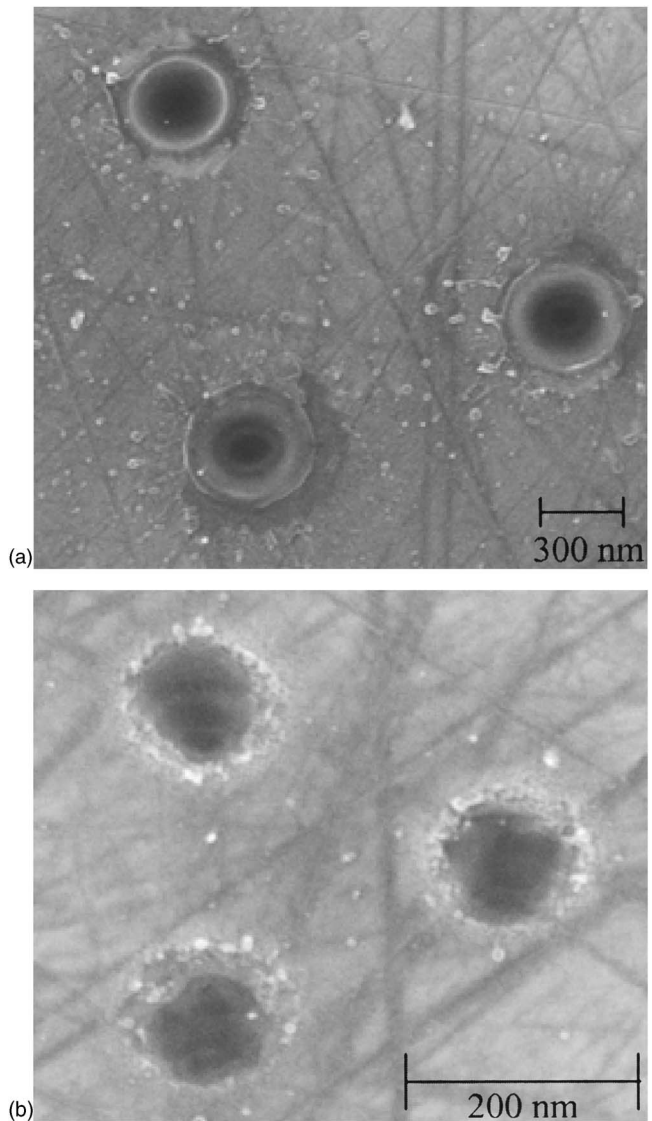


Fig. 3 Features formed on the SiC substrate with a 355-nm laser: (a) $1.76\text{-}\mu\text{m}$ -diam spheres and $950 \text{ mJ}/\text{cm}^2$, and (b) 640-nm -diam spheres and $850 \text{ mJ}/\text{cm}^2$.

2 Experimental Setup

The SiC substrate used in the experiment is a 6H-SiC polytype with a thickness of $368 \mu\text{m}$. The substrate is first cleaned in an ultrasonic bath with acetone and isopropanol. After drying the substrate with nitrogen, a colloidal suspension of monodispersed silica spheres are applied and allowed to dry. These spheres self-arranged themselves, forming a monolayer, confirmed by measurement using a scanning electron microscope (SEM) in Fig. 1.

The schematic of the experimental setup is shown in Fig. 2(a). The output laser beam is redirected by the harmonic separators and made smaller by using an aperture. By means of a plano-convex lens, the beam is then focused onto the sample, which is at the focal distance. The substrate is placed on an XYZ stage. The laser energies used in the experiment were measured using an energy meter. Figure 2(b) shows the schematic of the irradiation of a monolayer of silica nanospheres on the substrate.

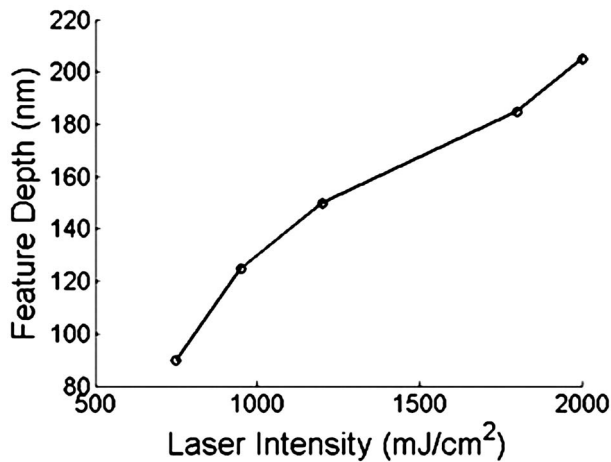


Fig. 4 Variation in the feature depth with respect to the laser intensity for 355-nm laser and 1.76- μm spheres.

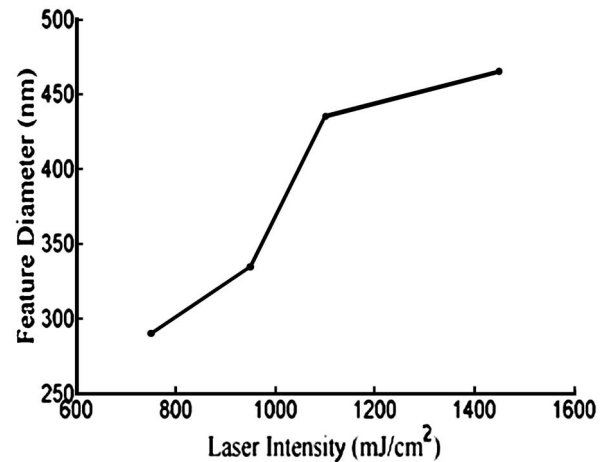


Fig. 5 Variation in the feature diameter with respect to the laser intensity for 355-nm laser and 1.76- μm spheres.

3 Results and Discussion

The experiments were conducted at different energies, and as predicted by the Mie theory, it was found that the minimum energy required for creating features on SiC is smaller for bigger spheres, irrespective of the laser wavelength. At a laser wavelength of 355 nm, the features started appearing at an incident energy density of 650 mJ/cm² for 1.76- μm spheres, whereas for 640-nm spheres, at least 850-mJ/cm² energy density is needed. This is because of the higher optical field enhancement for bigger spheres. However, in the absence of spheres, the actual threshold energy for substrate damage is found to be around 4 J/cm².

Figure 3 shows a SEM picture of the features obtained with laser wavelength 355 nm for both 1.76 μm and 640 nm spheres at 950 and 850 mJ/cm², respectively. The features are well defined for the 1.76- μm spheres compared to smaller spheres. The ablation mechanism for the formation of holes is discussed later in the section. Figure 4 shows the variation in feature depth with respect to the laser intensity for a 355-nm laser wavelength and 1.76- μm silica spheres. For the laser intensities used in our study, the depth increases with laser intensity from 90 to 210 nm. For the same conditions, Fig. 5 shows an increase in feature diameter from 300 to 450 nm, depending on the laser intensity. The different rate of increase in both the feature depth and diameter with laser intensity suggests that the interaction of the laser beam with the SiC substrate might be nonlinear.

Figure 6 is a scanning electron micrograph of the features obtained at a laser wavelength of 532 nm with 1.76- μm and 640-nm spheres at 2 and 6 J/cm², respectively. It is evident that SiC can be nanopatterned at 532 nm, despite the material being completely transparent to this wavelength. The initial energy needed for the formation of holes is around 2 J/cm² for 1.76- μm spheres and 5 J/cm² for the 640-nm spheres. Figure 7 shows the atomic force microscope data plot for the features obtained with 1.76- μm silica spheres. The feature diameters varied from 320 to 450 nm, and the depths varied between 100 to 175 nm, depending on the laser intensity.

The minimum feature diameter observed for both wave-

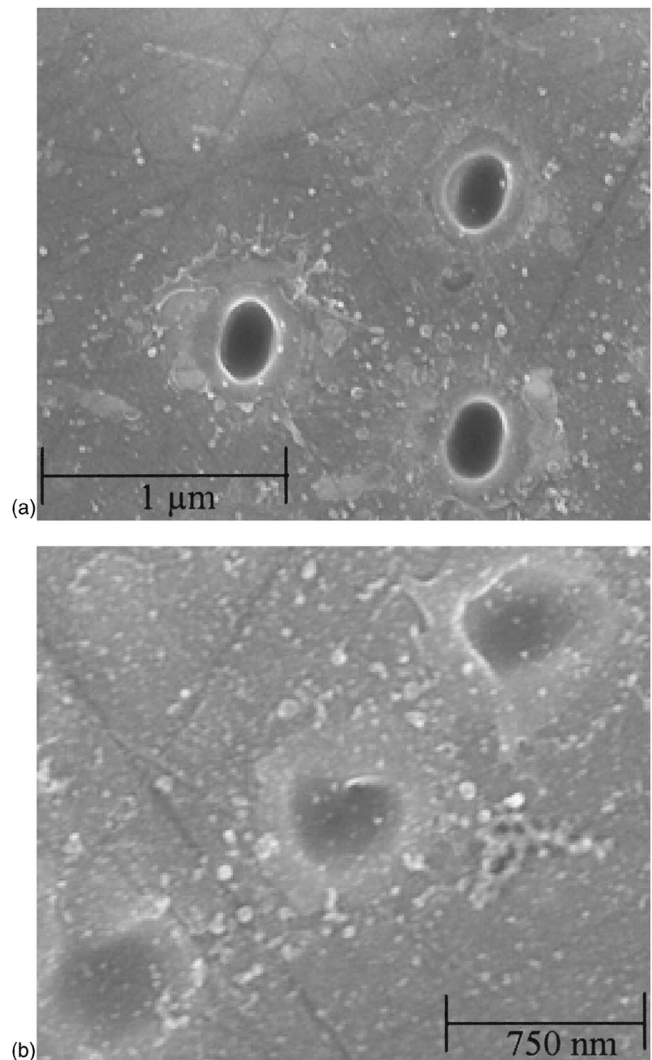


Fig. 6 Features formed on the SiC substrate with a 532-nm laser: (a) 1.76- μm -diam spheres and 2 J/cm², and (b) 640-nm-diam spheres and 6 J/cm².

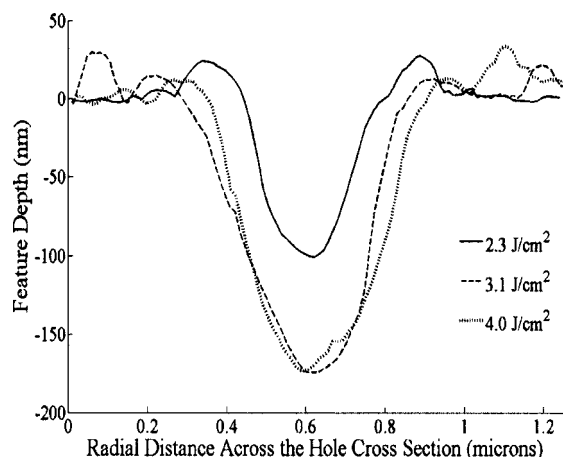


Fig. 7 AFM cross section view of the features obtained with a 532-nm laser and 1.76- μm spheres.

lengths is approximately the same, indicating a strong dependence on the bandgap energy of the material.¹⁴ Also, the depth of the features obtained with 355-nm wavelength is larger because of the higher absorption coefficient of SiC in the ultraviolet spectrum. From the prior discussions, it can be concluded that, for the ablation of SiC with 532-nm laser, higher intensity is required compared to the 355-nm laser. This is because the bandgap energy of SiC (6H-SiC polytype) is around 3.0 eV and the electron affinity is around 4.0 eV, which makes the minimum energy required for bond breakage near 7.0 eV. The photon energy of the 355- and 532-nm wavelength is approximately 3.49 and 2.32 eV, respectively. Therefore, to break the bonds using these wavelengths, the interaction has to be a multiphoton process, and hence very high intensities are required for the lower photon energy. Also, since SiC is transparent at 532-nm wavelength, the features formed could be due to the nonlinear interaction of the visible wavelength laser with SiC.

SiC is an indirect wide gap band semiconductor material and hence, due to multiphoton absorption, the electrons jump from the valence band to the higher energy levels of the conduction band. The possibility of an electron absorbing another photon in the conduction band is greater before becoming scattered with a phonon. Once the electron absorption of the photon takes place, the momentum is conserved by either plasmons or impurities or phonons. Therefore, whether the electron in the conduction band absorbs photons or not, the phonon energy increases with the number of electrons in the conduction band. This increase in phonon energy would lead to a lattice disorder that eventually would make bond breaking for ablation possible. The relation between the number of bond scissions and the excitation is linear when the bandgap energy is larger than the bond energy, otherwise, the relation is nonlinear due to the requirement of higher-order excitation energy.¹⁵

4 Conclusions

Nanopatterning of SiC material is achieved with features of diameter ranging from 150 to 450 nm, with depths ranging from 70 to 200 nm, depending on the laser energy. This kind of nanopatterning in a hard material like SiC is made

possible by using the optical near-field enhancement, obtained by the irradiation of silica spheres with a laser beam. The study demonstrates the possibility of nanopatterning transparent materials using nanosecond lasers by overcoming the diffraction limit of light. This study would open up the fabrication of new nanodevices having SiC as the main substrate. Applications include membrane of SiC with nanoholes for use in drug delivery and Schottky barrier diodes.

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Senthil Theppakuttai: biography and photograph not available.



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