UDK 546.28:621.791.725
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 57(5)459(2023)

WETTABILITY STUDIES ON FEMTOSECOND-LASER-TEXTURED N-TYPE SILICON SURFACES

ŠTUDIJ OMAKANJA POVRŠINE N-TIPA SILICIJA TEKSTURIRANE S FEMTOSEKUNDNIM LASERJEM

Vipparla Srikanth[1,2], G. L. Samuel[1*], Wei Dongbin[2]

[1]Indian Institute of Technology Madras, Chennai, India
[2]University of Technology Sydney, Australia

Prejem rokopisa – received: 2023-03-28; sprejem za objavo – accepted for publication: 2023-08-16

doi:10.17222/mit.2023.838

This present study examines the wetting behavior of N-type silicon surfaces that have been textured using a femtosecond laser. By employing three different patterns, i.e., square pillars, micro dimples, and circumferential grooves, and manipulating key femtosecond laser parameters such as laser power (ranging from 8 W to 12 W) and repetitions (ranging from 40 to 60), the wettability properties of the silicon surfaces are modified. The wettability properties of the surface were evaluated by measuring the contact angle by the sessile-drop method using distilled deionized water as a testing liquid. The textured surfaces displayed various wettability characteristics, varying from hydrophilic to hydrophobic. The hydrophobic behavior was observed on surfaces with a peak laser power of 12 W, 60 repetitions, and the lowest pitch of 160 µm. For the square pillar and micro-dimple textures, contact angles of 146° and 120°, respectively, were measured. Conversely, the circumferential grooves exhibited hydrophilic behavior with a contact angle of 20°. These results were achieved at laser powers of 10 W and 8 W, higher pitch values, and increased repetitions. The contact angle decreased with an increase in pitch and a decrease in repetitions and laser power. Based on the experimental findings, it can be concluded that the wettability of silicon surfaces can be controlled for specific applications using a single-step laser ablation technique. The desired wettability characteristics can be achieved by carefully adjusting the key femtosecond-laser parameters and geometrical features.

Keywords: wettability, texturing, femtosecond laser, hydrophobic, hydrophilic, silicon

Povzetek: avtorji v pričujočem članku opisujejo študijo oziroma preiskavo omakanja površine N-tipa silicija, ki so ga pred tem teksturirali s femtosekundnim (1 fs = $1 \cdot 10^{-15}$ s) laserjem. Z uporabo femtosekundnega laserja z močjo od 8 W do 12W in 40 do 60 ponovitvami so izdelali tri različne vzorce (kvadratne stebričke, mikronske jamice in krožne brazde oz. utore) in s tem spremenili oziroma modificirali omočljivost površine izbranega silicija. Omakanje površine so ovrednotili z merjenjem kontaktnega kota z metodo sesilne kapljice nastale na površini vzorca. Pri tem so kot preizkusno kapljevino uporabili destilirano deionizirano vodo. Medsebojne primerjave teksturiranih površin vzorcev so pokazale različno omakanje in sicer od hidrofilnega do hidrofobnega. Hidrofobno obnašanje kapljevine so zaznali na površinah z vršno močjo laserja 12 W in 60 ponovitvami ter najmanjšem koraku 160 µm. Pri teksturi s kvadratnimi stebrički so avtorji izmerili kontaktni kot oziroma kot omakanja 146° in pri teksturi z mikro jamicami 120°. Obratno pa so na teksturi s krožnimi brazdami opazili hidrofilno obnašanje s kontaktnim kotom 20° pri moči laserja 10 W in 8 W, višji globini jamic in večjem številu ponovitev. Ugotovili so, da se kontaktni kot zmanjšuje z naraščanjem globine teksture in z zmanjševanjem moči laserja ter števila ponovitev. Avtorji članka na osnovi eksperimentalnih ugotovitev zaključujejo, da se omakanje silicijeve površine za specifične aplikacije lahko kontrolira s pomočjo tehnike eno-stopenjske laserske ablacije. Željene karakteristike omočljivosti površine se lahko doseže s skrbno nastavitvijo ključnih parametrov femtosekundnega laserja in geometrijskih značilnosti.

Ključne besede: omočljivost, teksturiranje, femtosekundni laser, hidrofobno in hidrofilno obnašanje površin, polprevodniški silicij

1 INTRODUCTION

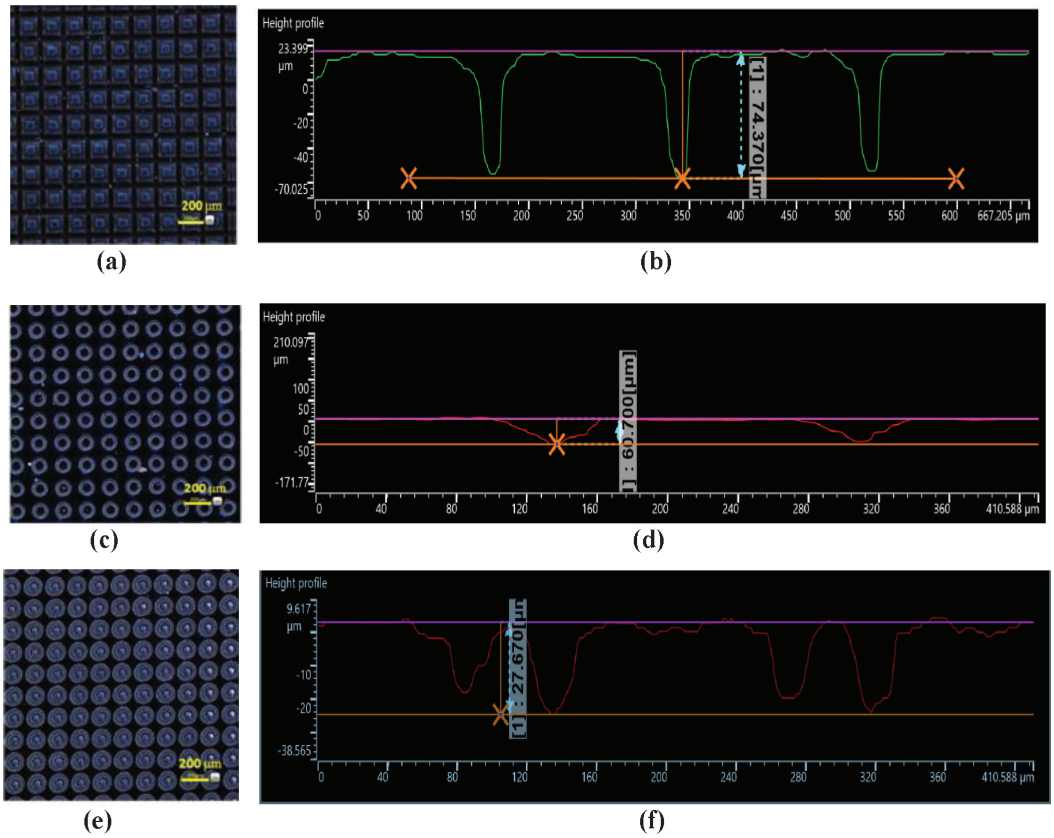
Silicon surfaces with unique wettability properties have a wide range of applications in intelligent sensors, microdisplays, gyroscopes, and miniaturized thermal radiation testers across various fields, such as sensing, biomedical, military, aerospace, and intelligent communications.[1] Normally, N-type silicon surfaces exhibit hydrophilicity with a contact angle of approximately 70–78°. However, their wettability properties can be modified by introducing physical structures or applying chemical coatings. Among these approaches, fabricating physical structures is preferred over chemical coatings as it preserves the surface chemistry and offers extended durability.[2] Various manufacturing methods can be used to obtain surface microstructures, including conventional photolithography, sandblasting, electrochemical techniques, powder spraying, and electron spinning. Among them, femtosecond-laser ablation is an efficient and rapid method for increasing surface roughness and creating micro-patterns.[3–7] Laser ablation allows for precise control in generating stable, three-dimensional (3D) surface structures, thereby enhancing superhydrophobic characteristics and potentially addressing the tribological issues in micro/nano-electromechanical (M/NEM) devices.[1] Zhu et al. investigated the generation of cross-pat-

*Corresponding author's e-mail:
samuelgl@iitm.ac.in (G. L. Samuel)

terned periodic structures on silicon surfaces through laser irradiation.[8] Wang et al. utilized pulsed-laser irradiation to fabricate textures on silicon surfaces, demonstrating that a combination of melting and surface evaporation could produce bump-like structures that can influence the contact angle.[9] Yang et al. combined laser texturing with silanization to create superhydrophobic surfaces on silicon materials. According to the Wenzel model, the intrinsic wettability of a solid surface is enhanced by increasing the surface roughness, meaning a hydrophilic surface becomes even more hydrophilic with an increase in average surface roughness.[1] Femtosecond- and nanosecond-laser ablation have been employed to generate various texture shapes such as lines, grids, and spots, as well as nanoscale laser-induced periodic surface structures (LIPSSs) and nanopillars with roughness distributions formed by overlapping LIPSS with micro-columns. By adjusting laser process parameters such as power and repetition rate, the wettability properties of surfaces can be significantly modified.[10,11] Considering the widespread use of N-type silicon wafers in different fields based on their wettability properties, it is essential to establish a comprehensive study that explores the effect of femtosecond-laser parameters and pattern shapes on the wettability of silicon surfaces. In this study, a single-step laser ablation process is employed to modify the wettability properties of the surface without altering its chemical composition, resulting in stable and chemically pure surfaces. Three geometrical shapes, namely square pillars, micro dimples, and circumferential grooves, are fabricated by varying the pitch, i.e., the distance between consecutive structures and laser operating parameters such as power and repetitions. The wettability of N-type silicon surfaces is observed to vary from near super-hydrophobic for high laser power and repetitions in the case of square pillar structures to near super hydrophilic for low power and repetitions in the case of circumferential grooves.

2 EXPERIMENTAL

The experiments are performed on a commercially available, N-type silicon wafer with a thickness of 0.5 mm. Samples were cleaned in an ultrasonic bath for 15 min using acetone before subjecting it to laser irradiation. A diode-pumped femtosecond-laser system (SATSUMA HP2, Amplitude Systems) with a central wavelength of 1030 nm, pulse duration of 350 fs, and pulse repetition rate of 2 kHz to 2 MHz was used for the surface treatment. The laser beam was directed to a set of x-y axes galvo scanning mirrors and then focused on the surface by a 250-mm focal length lens to a spot size of 120 μm, incident perpendicularly to the sample surface. The laser scanning was performed as per the pro-



(a) (b) (c) (d) (e) (f)

Figure 1: Topography of femtosecond-laser-textured surfaces: a) square pillars, b) height profile of square pillars, c) micro-dimples, d) height profile of micro dimples, e) circumferential grooves, f) height profile of circumferential grooves.

grammed path for the three patterns. As shown in **Table 1**, three levels for each parameter, i.e., laser power (12 W, 10 W, 8 W), pitch (160 µm, 190 µm, 220 µm), and repetitions (40, 50, 60), are considered. The micro-textures' topography and height profiles, as shown in **Figure 1**, were obtained by a 3D microscope, Olympus DSX 1000.

Table 1: The laser Processing Parameters considered for the experiments

Laser Power (W)	Pitch (µm)	Repetitions
8	160	40
10	190	50
12	220	60

The morphology of the laser-treated surfaces and XPS spectra indicating the chemical composition were analyzed by Inspect F50 Field Emission gun-based High-Resolution Scanning Electron Microscope (FESEM), presented in **Figures 2** and **7**. The contact angle, which characterizes the wettability of a surface, is evaluated by the sessile drop test using 5 µL of distilled deionized water as a testing medium at room temperature. The textured samples were first cleaned in an ultrasonic water bath, then the static contact angle on the surface was measured using a goniometer.

3 RESULTS AND DISCUSSION

3.1 Analysis of Surface Morphology

Figure 2 presents SEM images depicting laser-ablated surfaces with microns and nanostructures, individually or in combination. In **Figure 2a**, the structure exhibits a hierarchical arrangement of micro and nano features reminiscent of a lotus leaf, generating a roughness-induced hydrophobic effect. Notably, **Figures 2b**, **2f**, and **2j** illustrate that applying a laser power of 12 W leads to a concentration of higher fluence laser beams on the surface, resulting in greater material removal than surfaces treated with laser powers of 10 W and 8 W. This discrepancy is particularly evident in the micro-dimples de-

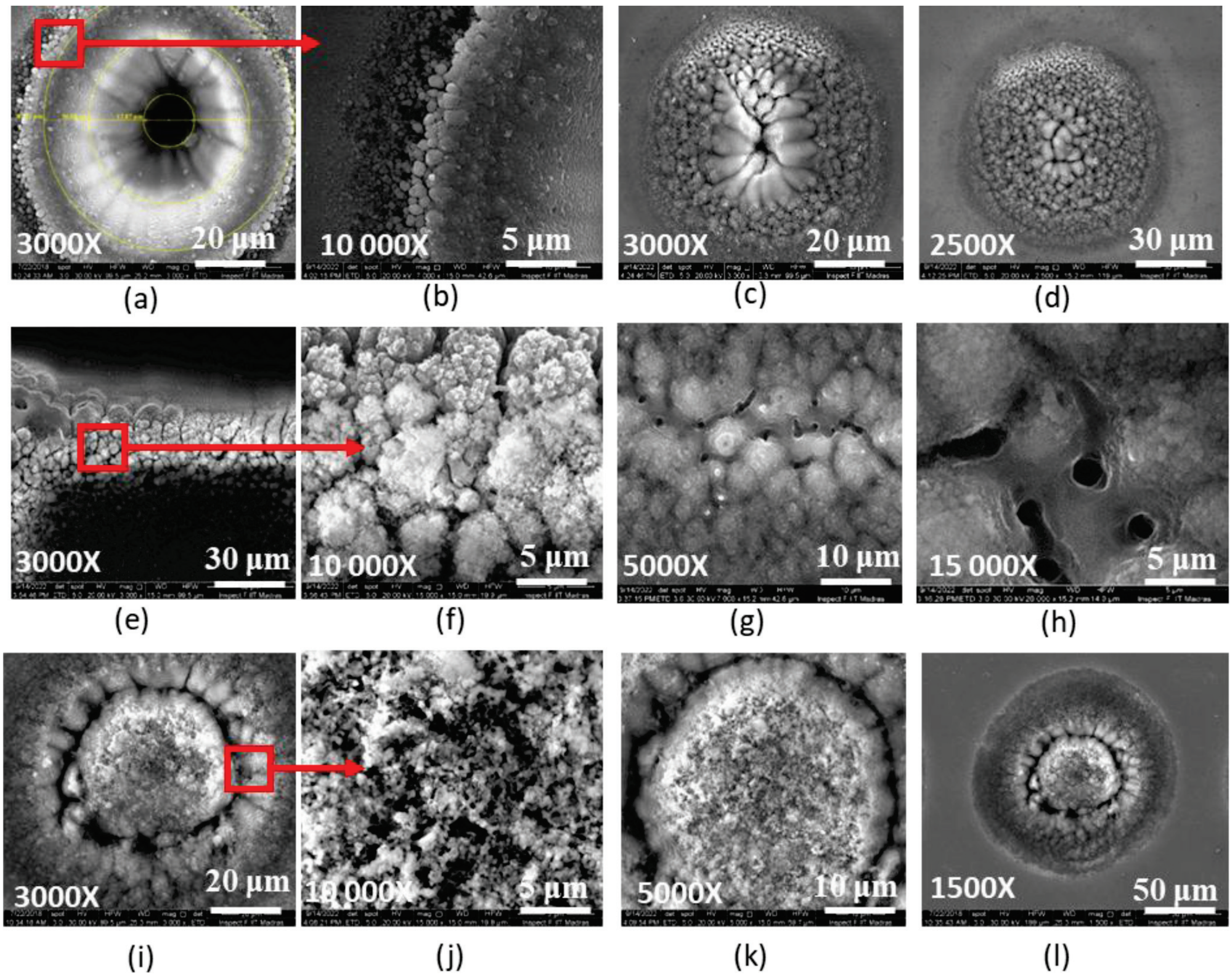


Figure 2: SEM Images of laser-treated surfaces: a) micro dimple at 12 W, b) outer layer of the micro dimple at 12 W, c) micro dimple at 10 W, d) micro dimple at 8 W, e) square Pillar at 12 W, f) outer layer of the square pillar at 12 W, g) Square pillar at 10 W, h) square pillar at 8 W, i) circumferential groove at 12 W, j) outer layer of circumferential groove at 12 W, k) circumferential groove at 10 W, l) circumferential groove at 8 W

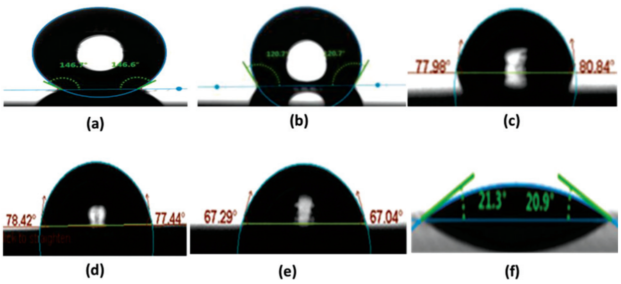


Figure 3: Contact angles of textured silicon surfaces: a) Square pillar at laser power 12 W, 60 repetitions, pitch 160 µm, b) Micro dimple at laser power 12 W, 60 repetitions, pitch 160 µm, c) Circumferential groove at laser power 10 W, 60 repetitions, pitch 160 µm, d) Micro dimples at 8 W, 40 repetitions, pitch 190 µm e) Square pillar at 10 W, 60 repetitions, pitch 190 µm f) Circumferential groove at laser power 8 W, 40 repetitions, pitch 220 µm

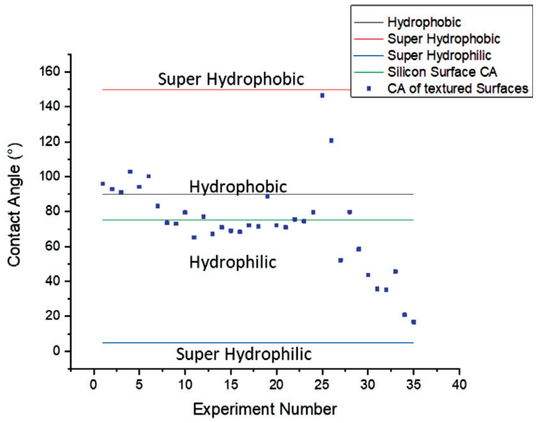


Figure 4: Spectrum of contact angles for the textured N-Type silicon surfaces

picted in **Figures 2b** and **2c**. Furthermore, when operating at 60 repetitions, the laser beam traverses the same path more frequently. Consequently, the bare silicon surface is exposed to laser treatment for an extended duration compared to 50 and 40 repetitions, leading to increased material irradiation. As the pitch decreases, the gap between the micro textures diminishes, resulting in the overlap of heat-affected zones.

3.2 Analysis of wettability of surfaces

Surface wettability can be characterized by measuring the contact angle, which allows for classifying surfaces as hydrophobic or hydrophilic. Figure 3 illustrates some of the contact angles observed on laser-textured surfaces. Asymmetry in the contact angle can arise due to surface heterogeneity, i.e., non-uniform surfaces with variation in chemical composition and roughness, surface contamination, i.e., presence of contaminants such as dust particles, oils, or residues, evaporation effects, i.e., evaporation of the liquid droplet occurs over time, and surface tension gradient. i.e., the surface tension of the liquid droplet may not be perfectly uniform across its interface. **Figure 3a** shows a nearly super-hydrophobic surface with a contact angle of 146°. This particular surface was achieved through a square pillar texture, utilizing a peak power of 12 W, 60 repetitions, and a pitch of 160 µm. Conversely, a nearly super-hydrophilic surface with a contact angle of 20° was observed on a circumferential groove pattern fabricated at a laser power of 8 W, 40 repetitions, and a pitch of 220 µm. A wide range of contact angles, from hydrophilic to hydrophobic, can be obtained using various combinations of laser parameters and pitch, as illustrated in **Figure 4**. It is worth noting that the laser power and repetitions directly influence the contact angle. **Figure 5** demonstrates that the contact angle usually increases with increased laser power and repetitions for all three patterns square pillars, micro-dimples, and circumferential grooves. Higher laser powers generally result in more significant changes to the surface topography, as they can lead to more pronounced surface roughness due to increased material removal or melting, subsequently contributing to the higher contact angle.

Figure 6 demonstrates the impacts of pitch and repetitions on the contact angle. The contact angle decreases as the pitch increases for all three patterns. This trend can be attributed to the widening gap between consecutive microtextures as the pitch increases. Consequently,

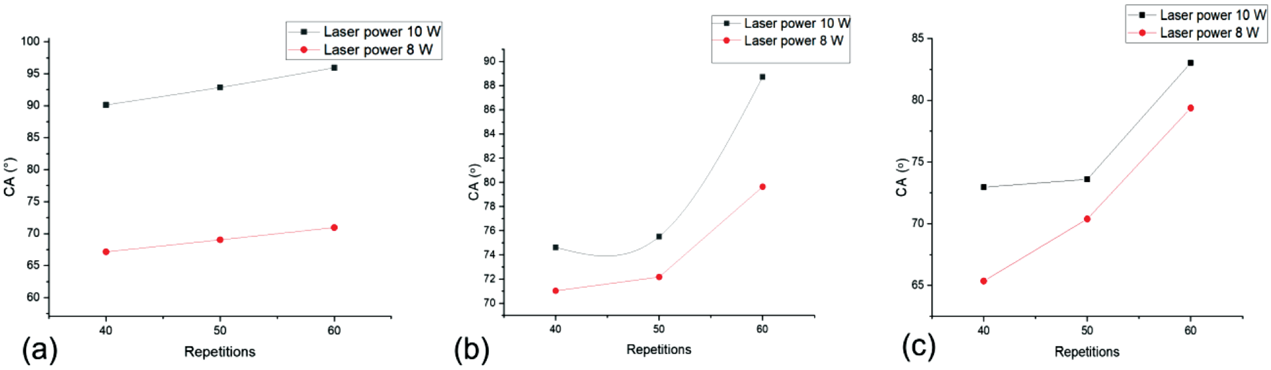


Figure 5: Influence of laser power and repetitions on the contact angle: a) square pillar at pitch 190 µm, b) micro dimples at pitch 190 µm, c) circumferential groove at pitch 190 µm

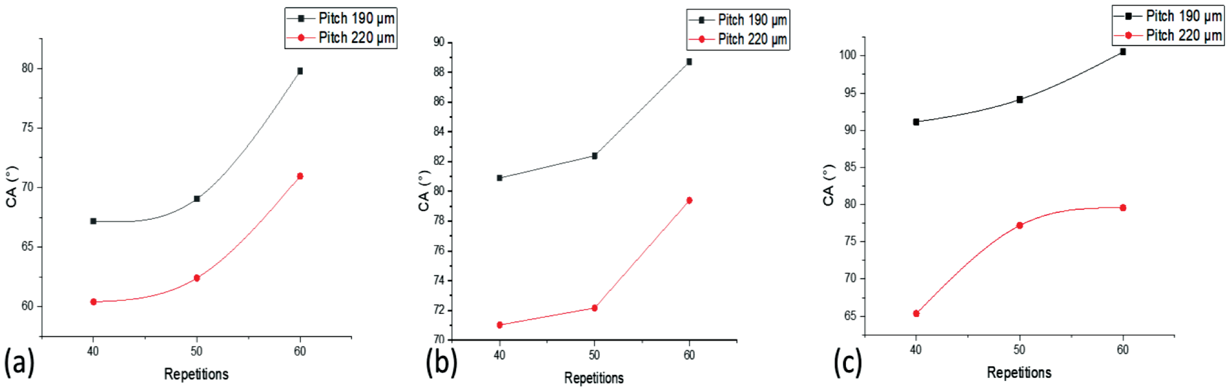


Figure 6: Influence of pitch and repetitions on the contact angle: a) square pillar at laser power 8 W, b) micro-dimples at laser power 8 W, c) circumferential grooves at laser power 8 W

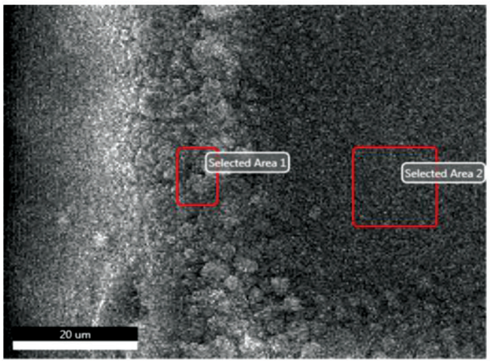
This reduction in surface roughness contributes to the overall decrease in the contact angle.

3.3 Analysis of Surface Chemical Composition

The XPS spectra of the laser-treated surfaces and a polished sample are depicted in **Figure 7**. The two spectra present peaks corresponding to silicon (Si) and oxygen (O) constituents. After laser treatment, the oxygen peak increases, which may result in the formation of silicon oxide (SiO_2), which is hydrophilic in nature. However, the thickness of the oxide layer influences the surface's wettability, a very thin oxide layer may be too rough or uneven to promote good wetting. At the same time, a very thick layer may be too smooth and prevent liquid from penetrating the surface.[8]

4 CONCLUSIONS

A novel, single-step laser-processing technique, requiring no additional post-processing steps, has been developed to fabricate a wide range of contact angles on N-type silicon, ranging from nearly super hydrophobic to hydrophilic. The study examines the influence of laser processing parameters, such as laser power and repetitions, and geometric parameters, such as texture shape



	Weight % of O	Weight % of Si
Area 1 (laser interaction zone)	48.6	51.4
Area 2 (Bare silicon)	15.4	84.6

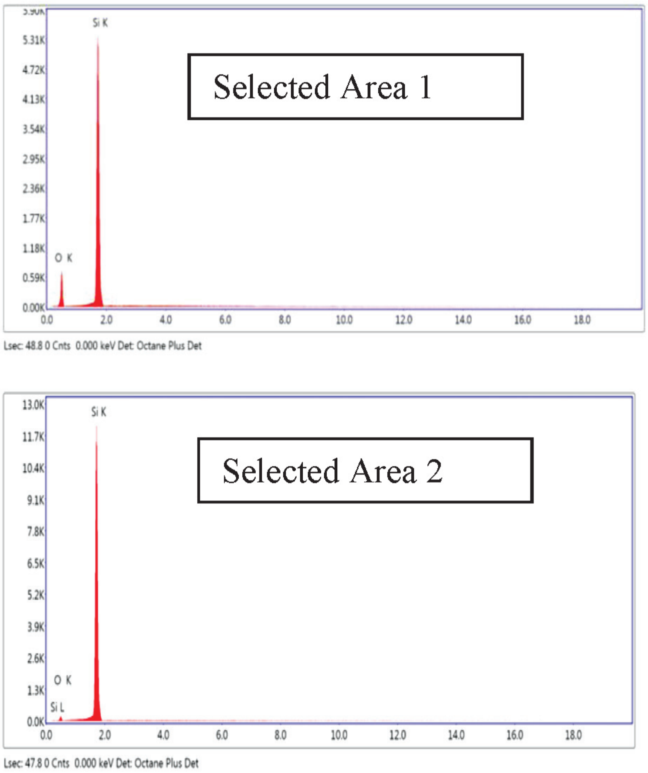


Figure 7: XPS Spectra indicating the chemical composition of the laser interacted zone and the non-interacted zone for square pillar texture at laser power 12 W, 60 repetitions, and pitch 160 µm

and pitch, on the wettability properties of N-type silicon. When utilizing square pillar and micro-dimple textures at a high peak power of 12 W and 60 repetitions, both textures effectively increase the contact angle of the silicon surface. This enhancement is particularly pronounced in the case of the square pillar texture, which covers a larger laser-processed area compared to the other two textures. Notably, the pitch of the texture exhibits an inverse relationship with the contact angle, while laser power and repetitions exert a direct influence. The findings of this study demonstrate the feasibility of creating both hydrophobic and hydrophilic stable surfaces on N-type silicon using femtosecond-laser processing. This advancement has significant implications for various industries, including sensing, biomedical and military applications, where precise control over surface wettability is crucial.

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