Black silicon technology and applications

Ali Shah
Black silicon technology and applications

Ali Shah

A doctoral dissertation completed for the degree of Doctor of Science (Technology) to be defended, with the permission of the Aalto University School of Electrical Engineering, at a public examination held at the lecture hall A205 (Otakaari 5, Espoo) on 9 November 2016 at 12:00.

Aalto University
School of Electrical Engineering
Department of Micro- and Nanosciences
Nanotechnology Group
Supervising professor
Professor Harri Lipsanen

Thesis advisor
Dr. Sami Suihkonen

Preliminary examiners
Professor Krisztian Kordas, University of Oulu, Finland
Dr. Michael Stenbæk Schmidt, Technical University of Denmark, Denmark

Opponent
Professor Jan Linnros, Materials Physics, ICT School, Royal Institute of Technology, Sweden
Abstract

This thesis focuses on fabrication, optimisation and integration of black silicon (bSi) for different applications. The research work presented in this thesis is divided into two parts. In the first part, bSi formation was studied in an inductively coupled plasma-reactive ion etcher (ICP-RIE). The design of experiments (DOE) technique was used to evaluate the influence of process parameters on bSi formation. The outcome was used to establish guidelines for fabricating different types of bSi. Applications of bSi are discussed in the second part of this thesis. Process development using standard and novel micro and nanofabrication techniques was performed to enable bSi employment for targeted applications. The developed processes were used to achieve patterned wetting of liquid droplets and a wide band optical enhancement. For patterned wetting, novel fabrication processes were developed to achieve patterns that composed extreme wetting contrast with the substrate. Hydrophobic, hydrophilic and superhydrophilic patterns were fabricated with superhydrophobic surroundings. Upon dispensing, the liquid droplets confined to more wettable patterns and mimicked their shape. Due to an extreme wetting contrast and topographical discontinuity, patterned wetting to a large number of patterns was achieved. A fabricated template containing patterns with extreme wetting contrast and topographical discontinuity with the surrounding substrate was used to demonstrate self-alignment of microchips. High accuracy, reliable and repeatable self-alignment of microchips was recorded. Several techniques were employed to improve the self-alignment of microchips on bSi based self-alignment template. Self-alignment of microchips is an increasingly popular technique for advanced packaging. Optical enhancement was achieved by optimisation of bSi surface structures. Improved anti-reflection and light trapping behaviour were demonstrated in UV-VIS spectrum. In order to extend the anti-reflection behaviour of bSi beyond UV-VIS, conformal pyrolytic carbon (PyC) coating was deposited and a substrate with exceptionally low reflectance over a wide spectrum (UV-NIR) was achieved. The surface structure optimisation was also exploited for plasmonic enhancement. Thin silver (Ag) films and different bSi surface structures were studied to achieve highly sensitive surface-enhanced Raman spectroscopy (SERS) substrate.

Keywords  black silicon, deep reactive ion etching, droplet confinement, optical enhancement

ISSN (printed) 978-952-60-7112-1  ISBN (pdf) 978-952-60-7111-4
Preface

The research work presented in this thesis was carried out in the Nanotechnology group of the Department of Micro- and Nanosciences at Aalto University under the supervision of Professor Harri Lipsanen.

Firstly, I would like to express my sincere and deepest gratitude to Professor Harri Lipsanen for providing the work opportunity and supervising the thesis. I will always be grateful for the freedom, support, valuable advice, great work environment and the resources you made available to me. All these years, I had the privilege to work on very interesting and exciting projects. I also want to thank you for all the help, support, and advice towards my professional career.

I would like to acknowledge and thank my instructor Dr. Sami Suihkonen for his guidance throughout my academic career. I would like to thank Dr. Ville Jokinen and Professor Sami Fransson from the department of Material Science and Technology at Aalto University and Dr. Lauri Sainiemi for their expertise in microfabrication and microfluidics. I thank Micro and Nanorobotics group at Aalto University for their collaboration. I am especially thankful to DI Ville Liumatainen and Dr. Bo Chang for a productive collaboration. I would like to thank Dr. Tomi Kaplas from Institute of Photonics University of Eastern Finland for a memorable and friendly collaboration. I am also grateful to Aalto Nanofabrication center at Micronova for all the help to keep everything running smoothly. I would like to express my gratitude to Dr. Victor Ovchinnikov for introducing me to the world of silicon micro and nanofabrication and sharing his wealth of experience and knowledge.

Over the years, I was fortunate to work with the best at Micronova and for that, I am grateful to everyone. Many have moved on from their academic careers and I would like to wish them the best for the future. I am in debt to my former colleagues, Dr. Lasse Karvonen, DI Olli Svensk, Dr. Marco Mattila, Dr. Ya Chen, Dr. Muhammad Ali, Dr. Pekka Törmä, Dr. Nikolai Chekurov, DI Pasi Kostamo, Dr. Henri Nykänen, Dr. Sakari Sintonen, and Dr. Juha Riikonen for sharing their experience and knowledge with me. I want to thank Dr. Sami Kujala, DI Ville Pale, Dr. Antti Säynätjoki, Dr. Lauri Riutinanen, Dr. Alex Perros, Dr. Tuomas Haggrén, Dr. Nagrangan Subramaniym, Dr. Henri Jussila, DI Joona-Pekko Kakko, Dr. Veer Dhaka, DI Anton Autere, DI Joonas Mäkinen, DI Mikko Ruoho, DI Christoffer Kauppinen, DI He Yang, DI Perttu Sippola, and DI John Rönn for all the time we shared together. I wish you all...
the best for your future endeavors. I would like to thank Dr. Tapani Alasaarela for the work we have done together. I have enjoyed our discussions and learned a lot from you. I thank Professor Ilka Tittonen, Professor Zhipei Sun, Professor Markku Sopanen and Hanne Ludvigsen for friendly discussions and advice over the years. I want to thank Dr. Kuan Yen Tan for all those discussions and EBL related help.

I would like to thank my friends Clara, Tatiana, Laura, Efi, Sergey, Zubi, Ashu, Sunil, and Ana for all the help, support, and friendly presence all these years.

Finally, I wish to thank my better half Leticia for everything. You have been a source of inspiration, a motivation and the reason that I have made it this far. I thank you for your faith in me, all the support and love.

Vantaa, October 9, 2016,

Ali Shah
### Contents

- List of Abbreviations and Symbols .......................................................... v
- List of Publications ................................................................................ vii
- Author’s Contribution ............................................................................. ix

1. **Introduction** ................................................................................... 1
2. **Black silicon** .................................................................................. 3
   2.1 **History** ...................................................................................... 3
   2.2 **Fabrication methods** ................................................................ 5
   2.3 **Material properties** .................................................................. 11
   2.4 **Uses** .......................................................................................... 17
3. **Experimental techniques** .................................................................. 19
   3.1 **Deposition** ................................................................................ 19
   3.2 **Patterning** ............................................................................... 20
   3.3 **Etching** ..................................................................................... 21
   3.4 **Characterization** ....................................................................... 23
4. **Results and applications** ................................................................. 25
   4.1 **Fabrication of bSi** .................................................................... 25
   4.2 **Patterned wetting** .................................................................... 30
   4.3 **Optical enhancement** .............................................................. 40
5. **Summary and outlook** ..................................................................... 47

**References** .............................................................................................. 49
### List of Abbreviations and Symbols

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>atomic force microscope</td>
</tr>
<tr>
<td>ARC</td>
<td>anti-reflection coating</td>
</tr>
<tr>
<td>BHF</td>
<td>buffered hydrofluoric acid</td>
</tr>
<tr>
<td>bSi</td>
<td>black silicon</td>
</tr>
<tr>
<td>CA</td>
<td>contact angle</td>
</tr>
<tr>
<td>CCP</td>
<td>capacitively coupled plasma</td>
</tr>
<tr>
<td>CHF$_3$</td>
<td>trifluoromethane</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapour deposition</td>
</tr>
<tr>
<td>DOE</td>
<td>design of experiments</td>
</tr>
<tr>
<td>DRIE</td>
<td>deep reactive ion etching</td>
</tr>
<tr>
<td>EM</td>
<td>electromagnetic</td>
</tr>
<tr>
<td>ESEM</td>
<td>environmental scanning electron microscope</td>
</tr>
<tr>
<td>FE</td>
<td>field emission</td>
</tr>
<tr>
<td>HBr</td>
<td>hydrogen bromide</td>
</tr>
<tr>
<td>HF</td>
<td>hydrofluoric acid</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>nitric acid</td>
</tr>
<tr>
<td>ICP</td>
<td>inductively coupled plasma</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>MEMS</td>
<td>microelectromechanical systems</td>
</tr>
<tr>
<td>NIR</td>
<td>near-infrared</td>
</tr>
<tr>
<td>PECVD</td>
<td>plasma enhanced chemical vapour deposition</td>
</tr>
<tr>
<td>PIII</td>
<td>plasma immersion ion implantation</td>
</tr>
<tr>
<td>PyC</td>
<td>pyrolytic carbon</td>
</tr>
<tr>
<td>R6G</td>
<td>rhodamine 6G</td>
</tr>
<tr>
<td>RIE</td>
<td>reactive ion etching</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>SERS</td>
<td>surface enhanced Raman scattering</td>
</tr>
<tr>
<td>SF$_6$</td>
<td>sulphur hexafluoride</td>
</tr>
<tr>
<td>SiH$_4$</td>
<td>silane</td>
</tr>
<tr>
<td>SPR</td>
<td>surface plasmon resonance</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>VIS</td>
<td>visible</td>
</tr>
<tr>
<td>XPS</td>
<td>x-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>$f$</td>
<td>fraction of solid</td>
</tr>
<tr>
<td>$H$</td>
<td>height of black silicon</td>
</tr>
<tr>
<td>$L_c$</td>
<td>correlation length</td>
</tr>
<tr>
<td>$n$</td>
<td>refractive index</td>
</tr>
<tr>
<td>$r$</td>
<td>roughness factor</td>
</tr>
<tr>
<td>$t$</td>
<td>etch depth of silicon</td>
</tr>
<tr>
<td>$w$</td>
<td>width of black silicon</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>interface free energy</td>
</tr>
<tr>
<td>$\theta_{a}$</td>
<td>apparent contact angle</td>
</tr>
<tr>
<td>$\theta_{c}$</td>
<td>critical contact angle</td>
</tr>
<tr>
<td>$\theta_{e}$</td>
<td>equilibrium contact angle</td>
</tr>
<tr>
<td>$\theta_p$</td>
<td>angle of topographical boundary</td>
</tr>
<tr>
<td>$\theta_Y$</td>
<td>Young’s contact angle</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>wavelength</td>
</tr>
</tbody>
</table>
List of Publications

This doctoral dissertation consists of a summary of following publications which are referred to in the text by their numerals


2. Shah, Ali; Chang, Bo; Suihkonen, Sami; Zhou, Quan; and Lipsanen, Harri. 2013. Surface-tension driven self-alignment of microchips on black silicon based hybrid template in ambient air. Journal of Microelectromechanical Systems, volume 22, issue 3, pages 739-746. DOI: 10.1109/JMEMS.2013.2243109


4. Chang, Bo; Shah, Ali; Zhou, Quan; Ras, Robin; and Hjort, Klas. 2015. Self-transport and self-alignment of microchips using microscopic rain. Scientific Reports, volume 5, number 14966. DOI: 10.1038/srep14966

5. Liimatainen, Ville; Shah, Ali; Johansson, Leena-Sisko; Houbenov, Nikolay; and Zhou, Quan. 2016. High-precision, persistent and extreme wetting-contrast patterning in an environmental scanning electron microscope. Small, volume 12, issue 14, pages 1847-1853. DOI: 10.1002/smll.201503127

6. Shah, Ali; Stenberg, Petri; Karvonen, Lasse; Ali, Rizwan; Honkanen, Seppo; Lipsanen, Harri; Peyghambarian, Nasser; Kuitinen, Markku; Svirko, Yuri; and Kaplas, Tommi. 2016. Pyrolytic carbon coated black silicon. Scientific Reports, volume 9, number 25922, DOI: 10.1038/srep25922
7. Chen, Ya; Kang, Guoguo; Shah, Ali; Pale, Ville; Tian, Ying; Sun, Zhipei; Tittonen, Ilkka; Honkanen, Seppo; and Lipsanen, Harri. 2014. Improved SERS intensity from silver-coated black silicon by tuning surface plasmons. Advanced Materials Interfaces, volume 1, issue 1, number 1300008, DOI: 10.1002/admi.201300008
Author’s Contribution

Publication 1: Non-reflecting silicon and polymer surfaces by plasma etching and replication

The author performed design of experiments (DOE), fabrication and characterization of black silicon. The author analysed the data and contributed towards the section of manuscript related to black silicon fabrication and optimization.

Publication 2: Surface-tension driven self-alignment of microchips on black silicon based hybrid template in ambient air

The author wrote the manuscript for this publication. The author designed the fabrication process, performed the fabrication, sample characterisation and analysed the data.

Publication 3: Surface-tension driven self-assembly of microchips on hydrophobic receptor sites with water using forced wetting

The author designed and fabricated the self-alignment templates. The author performed the characterization of fabricated samples and contributed to the section of manuscript related to template fabrication.

Publication 4: Self-transport and self-alignment of microchips using microscopic rain

The author designed the fabrication process for self-alignment template. The author performed the surface characterization of fabricated samples and contributed to the writing of the manuscript.

Publication 5: High-precision, persistent and extreme wetting-contrast patterning in an environmental scanning electron microscope

The author designed the fabrication process for fluorinated and parylene coated black silicon. The author characterised the fabrication process and contributed to the writing of the manuscript related to black silicon and parylene.

Publication 6: Pyrolytic carbon coated black silicon

The author wrote the manuscript for this publication. The author fabricated
the black silicon, characterized the samples and performed the reflectance measurements.

**Publication 7: Improved SERS intensity from silver-coated black silicon by tuning surface plasmons**

The author performed the optimisation and fabrication of black silicon. The author contributed to the writing of manuscript related to the fabrication of black silicon.
1. Introduction

Black silicon is a modified silicon (Si) surface, composed of densely packed and randomly distributed micro and nanostructures. For a broad spectrum of incoming light, the micro and nanostructures enhance scattering and absorption, whereas the reflection is significantly suppressed. As a consequence, the silicon surface appears black to the naked eye and the material is often called black silicon (bSi). Due to the surface topography, it has also been named as silicon grass, micrograss, nanospikes, nanoneedles, nanograss, nanowhiskers etc.

For several reasons, bSi observed during reactive ion etching (RIE) of Si was widely considered a major drawback of dry etching. Firstly, the desired smooth etch profile was replaced by highly unwanted randomly distributed bSi micro and nanostructures. Secondly, the influence of process parameters leading to bSi rather than a smooth etch profile was still unclear. Thirdly, bSi produced in an RIE was not pursued for potential applications even though Si surface texturing using sputter etching was demonstrated for enhanced light absorption even before bSi formation in RIE. [1] The potential of bSi produced in an RIE was unclear and therefore bSi was considered a more common RIE nuisance.

In a detailed study called black silicon method, it was established that bSi regime can be found by variation and optimisation of process parameters. [2] The approach highlighted the influence of process parameters on bSi formation and suggested strategies to avoid bSi and achieve smoother Si etch profile. In terms of applications, bSi as a material gathered more interest upon its discovery under concentrated laser pulses. [3] The bSi formation over a large area was repeatable and the technique allowed control of shape and frequency of spikes. The fabricated structures showed promising optical behaviour and opened doors to a widespread interest. Since then, a plethora of dry and wet etching techniques have been developed for the fabrication of bSi micro and nanostructures.

The surface structures of bSi enable many attractive properties that are superior to plain Si. For a broad spectrum of incoming light (UV-VIS), the reflection is remarkably suppressed. Such behaviour is beneficial for enhanced light absorption and also for the potential use of bSi as an antireflection coating (ARC). The remarkable optical response can be extended to higher wavelengths (NIR and above) by either incorporating dopants during fabrication or post fabrication integration of other materials. The interaction
of light can be also varied by optimising the surface structures. Relatively smaller features of bSi can be combined with noble metals (gold (Au) and silver (Ag)) to excite the surface plasmons and achieve surface-enhanced Raman scattering (SERS). This approach is useful to achieve large area SERS substrates for biosensors.

Compared to plain Si surface, the structural topography and hierarchy of bSi surface provide a possibility to tailor the interaction of liquids, especially water. By changing the surface chemistry of bSi, different wetting, and non-wetting regimes can be achieved, i.e. hydrophilic, hydrophobic, superhydrophilic and superhydrophobic. Furthermore, these regimes can be achieved side by side onto the same substrate using the standard fabrication techniques. The behaviour of droplet varies in different wetting regimes and a patterned wetting can be realised. Patterned wetting offers self-guiding, self-positioning, self-alignment and manipulation of water droplets. These are particularly useful characteristics for droplet microfluidics.

This thesis presents results of bSi technology that can be divided into two parts: fabrication and optimisation of bSi and applications of bSi. The former involves the design of experiments (DOE) using Taguchi method to study the influence of process parameters on bSi formation (Publication 1). The latter part of the results is divided into two areas of applications: patterned wetting and optical enhancement. Photolithographic and direct patterning techniques are developed to achieve the patterned wetting of water droplets. Photolithographically patterned wetting is used to demonstrate self-alignment of microchips (Publications 2-4). Patterned wetting using direct writing is achieved using electron beam in an environmental scanning electron microscope (ESEM) in the presence of water vapour (Publication 5). For optical enhancement, pyrolytic carbon coating is deposited and bSi substrate with exceptionally low reflectance over a wide spectrum (UV and NIR) is demonstrated (Publication 6). The results also include bSi structure optimisation for SERS where thin Ag films are evaluated for a substrate with high SERS activity (Publication 7).
This chapter begins with the history of bSi. This is followed by a brief introduction to different fabrication techniques. Dry etching based fabrication techniques are presented afterwards where reactive ion etching (RIE) based fabrication techniques are discussed in detail. Following these discussions, properties of bSi relevant to the scope of this thesis are introduced. At the end of this chapter, uses of bSi for different applications are highlighted.

2.1 History

In early 1980’s, the results of silicon RIE showed considerable variation and pronounced roughness across the silicon wafer. The recorded etch rates were unusual with a constant compromise on uniformity and in some cases, the majority of the sample surface was covered with darker spots. The formation of surface roughness after RIE transformed the Si surface from silver-grey like surface to black and therefore was referred to as black silicon (bSi). [7] As etching of deep trenches in silicon using RIE was increasingly important for a vast majority of applications, superior etch profiles with minimum roughness were expected. Micromasking by photoresist masks, insulating oxides, and metal re-deposition during RIE were considered traditional causes of surface roughness on silicon. Different techniques of surface modification, including pre-RIE cleaning/conditioning and post-RIE processing were used to reduce the surface roughness. In spite of the preconditioning and cleaning precautions, the surface roughness was observed. The post RIE techniques for roughness elimination stacked additional process steps, which introduced complexities and additional costs. Logically, a better understanding of the bSi formation was needed, whereas the knowledge and influence of RIE process parameters for bSi formation were missing. Improved etch surface profiles were needed and therefore the post RIE techniques to overcome bSi were unavoidable. The ever growing importance of Si RIE led to detailed studies for RIE process improvement. In investigations, aiming at improved RIE process parameters for silicon etching, it was discovered that the process parameters strongly influence the bSi formation. Under certain RIE process conditions, the bSi formation was promoted and affected overall etching of Si. The nature of Si RIE process contributed to bSi and to overcome the problem and achieve smooth, anisotropic and selective Si etch profiles, careful RIE process optimisation was needed.
The relationship between the RIE process parameters and bSi formation was used to demonstrate black silicon method, a technique to avoid black Si and find reliable process parameters for an arbitrary RIE. [2] The technique highlighted the influence of process parameters and suggested strategies overcome the bSi formation during RIE. Although black silicon method was initially developed for deep and smooth RIE of silicon, it was also found that the method can be adopted to establish guidelines for RIE of other materials. [10] The black silicon method provided the guidelines to avoid bSi and an ability to control Si etching profile for a wide range of features. The method is widely known and well documented with a detailed account of complete RIE process parameters. [2][10][11][12][13]

As bSi became a commonly known side effect of RIE, the focus was to avoid bSi and obtain the smooth Si etch. Although, the earliest studies suggested bSi for AFM tips and laser components [2], the material was not pursued for a potential application. Other than a side effect, bSi caught more attention when it was accidentally discovered in a different technique. Using the similar process gases as RIE, bSi was observed under concentrated laser pulses. [3] The bSi formation was demonstrated over a large area and the process was repeatable. The technique allowed control of the shape and frequency of spikes and offered insight into the influence of process parameters on bSi.

The new fabrication technique raised the scientific interest for potential applications, i.e. light absorber for solar cells and photodetectors, and as microneedles for microfluidics. [14][15][16] Versatile nature of the material and demonstrated applications assisted in the popularity of bSi. Widespread scientific interest led to a change of perspective from a side effect of RIE to a promising material.

While the existing techniques for bSi fabrication were constantly improved, the applications of the material were expanding to new disciplines. A widespread interest catalysed the development of new techniques for bSi fabrication. Wet etching techniques were utilised to structure the Si surface and as a result large area silicon nanostructures were achieved. [17][18][19] These techniques were simple, flexible and offered alternative possibilities for Si surface texturing for solar cells application. Furthermore, a combination of different techniques has also been used to demonstrate densely packed ordered nanostructures over a large area. [20][21][22]

The focus on fundamental properties of bSi and growth as a material as seen a remarkable rise over the last decade. Extensive studies have contributed to a widespread understanding of the nature of the material. Considering that not long ago, the material was considered a side effect of dry etching, the scale of demonstrated applications is phenomenal. The properties of bSi have improved and helped a lot in realising applications for different disciplines. Integration with new materials and incorporation of new techniques is opening new possibilities and applications. Currently popular for energy applications, the nanostructured bSi is also becoming an interesting platform and starting substrate for other applications. Due to a large chemically active
surface area, bSi is very promising as a support platform for a wide range of chemical and physical reactions. [23]

### 2.2 Fabrication methods

A wide range of bSi fabrication methods have been developed over the last two decades. These fabrication techniques offer flexibility and a range of compatible materials. The techniques of bSi fabrication fall into major categories of wet etching, laser ablation and reactive ion etching. The fabrication techniques using wet and laser ablation will be briefly described, as the details of those methods are not subject of the work performed in this thesis. Reactive ion etching will be introduced and explained in detail.

#### Wet etching

For wet fabrication of bSi, electrochemical etching, stain etching and metal assisted etching techniques are used. In an electrochemical etching process, Si is oxidised in H$_2$O medium and subsequently removed by hydrofluoric acid (HF) under an applied current and/or illumination. [24] Under controlled circumstances, this process leads to randomly distributed nanopillars. [25] The process is low cost and compatible with standard microelectronic fabrication. Large scale industry adoption is a big challenge due to nature of current driven etching process. [23]

In stain etching, nitric acid (HNO$_3$) and HF mixture is used to structure the Si surface. Having the same function as H$_2$O in the electrochemical etching process, HNO$_3$ oxidizes Si, whereas HF dissolved the oxidised Si. [26] Due to similarity to the electrochemical etching process, stain etching is often called localized electrochemical etching. However, the technique is rather unpopular due to the fast surface removal of Si and reduced height of structured layer.

In the presence of nanoparticles of noble metals, smooth Si surface can be transformed into micro and nanostructures by HF and an oxidizing agent. [19] Gold (Au) and silver (Ag) are typically used as catalysts and the process is commonly referred to as metal-assisted chemical etching. During the process, Si is oxidised underneath the metal nanoparticles and subsequently removed by HF. [27] The selective removal of Si sinks the nanoparticles into the Si and forms nanostructures. The height of the nanostructures is controlled by the etching time. [28] Metal-assisted chemical etching is a versatile etching technique with an ability to control the morphology of the nanostructures. The technique is increasingly popular and is constantly gathering interest. [23]

#### Laser ablation

In laser ablation technique for fabricating bSi, Si wafer is irradiated with femtosecond-laser (fs-laser) pulses in a reactive or non-reactive gases
environment. [3][14] The bSi formation is a result of both laser ablation and laser-induced chemical etching. During a fs-laser treatment, the Si substrate lacks thermal equilibrium due to excitation of a large fraction of electrons from valence band to conduction band. [29] The lack of thermal equilibrium leads to rapid disorder of the lattice and the mechanism is responsible for morphological changes in Si surface. [23]

In the early stages of the fs-laser treatment, the capillary waves created in molten Si form sub-micrometre sized ripples structure. [30] After that, coarser micrometre-scale ridges open on top of the ripples form a surface layer. With time, the surface layer with ridges evolves into micrometre-sized beads. The shape and size of the beads define the final shape of the spikes which can differ one to two orders of magnitude, depending on the medium of the fs-laser treatment. [31]

The nature of created spikes can be tuned by changing laser parameters, ambient medium, and process gases. The laser parameters define interaction time with Si, energy delivered to Si and ablation rate of Si. [32][33] The parameters influence the height of spikes and their overall topography (micro and nanostructuring). The medium of laser treatment affects the overall size of bSi spikes and extremely small spikes are observed in liquid media. [31] The change in size is a result of the difference in capillary waves on molten Si surface combined with the laser-induced etching.

Process gases used during fs-laser treatment have a strong influence on the nature of the spikes. Tall, conical and sharp spikes can be produced in a reactive environment, whereas non-reactive atmosphere (vacuum, N₂, He) results in blunted structures. [3] [34] The reactivity of the halogen gases with Si is well known and therefore, the influence of the process gases is of chemical nature. The presence of high-intensity fs-laser pulses enhances the reactivity of etching gas, producing etching radicals and liquefying Si, which can be etched by chlorine (Cl₂). [3]

In a reactive gas environment, e.g. SF₆, the additional benefit arises from the incorporation of sulphur and other structural defects in Si lattice. These defects combined with the nanostructured surface offers sub-band absorption, which cannot be achieved in a non-reactive gas environment. [15] The formation of sulphur doping extends the working window of bSi to IR and the heavily sulphur doped Si can also be used for intermediate band photovoltaics. The photoresponsivity of sulphur doped bSi improves with annealing and photodiode with superior properties has been demonstrated. [15][35] Also, sulphur doped bSi is luminescent upon annealing, and the luminescent wavelength can be tuned with different annealing temperatures. [36]

The fs-laser pulses induce damage to the Si and the bSi surface is electronically less active after the treatment. Post-annealing is often needed to improve carrier mobility. [35] However, the annealing temperature window needs careful control without compromising electronic response, sub-band gap absorption and photoresponse. The fs-laser process for bSi is slower in comparison with other fabrication techniques. Also, the laser-induced damage
is quite significant and clearly a drawback where superior material quality is needed.

**Reactive ion etching**

Formation of bSi in RIE has a long history and a wide range of RIE strategies to fabricate bSi has been demonstrated. The first RIE study highlighting the influence of process parameters on bSi was reported as black silicon method using sulphur hexafluoride (SF₆) and oxygen (O₂) gas chemistries. [2]

Typically, in SF₆/O₂ RIE of Si, the radio frequency (rf) plasma breaks SF₆ and forms SFₓ ions and F* radicals and O₂ to form O* radicals. The F* radicals diffuse towards the substrate and a reaction with Si produces volatile SiFₓ products causing isotropic Si etch. Simultaneously, the O* radicals diffuse towards the substrate and form a passivation layer of SiₓOᵧFz, that protects the Si surface. [2] The SiₓOᵧFz passivation layer is not etched by F* radicals, however, it is prone to physical directional etching by SiFₓ ions. The directional bombardment of SiFₓ ions removes the SiₓOᵧFz layer from the horizontal surface and F* radicals etch Si, whereas, the SiₓOᵧFz layer on the sidewalls stays unharmed and protects Si from etching.[7] This competition between etching and passivation leads to anisotropic etching of Si, shown in Figure 1, where the etch rate increases with rf power.

![Figure 1. RIE of Si in SF₆ and O₂ gas chemistry. [2]](image)

The competition between passivation and etching can also cause rapid self-masking and etching on a horizontal surface. The self-masked areas are protected, whereas the surroundings are etched and the process leads to the formation of random micro and nanostructures, shown in Figure 2. [2][23] To avoid self-masking leading to bSi, guidelines suggested in black silicon method are used. The guidelines are useful for finding parameters set for an arbitrary RIE system.[2] In black silicon method, RIE of Si is performed in SF₆ and O₂ is added in steps until bSi is formed. At this stage, if the purpose is to avoid bSi, SF₆ and O₂ flows are fixed and trifluoromethane (CHF₃) gas is added in steps until bSi disappears. The role of CHF₃ is to provide CFₓ ions that etch SiₓOᵧFz directionally by forming volatile compounds, shown in Figure 2b.

During etching, the self-masking regions are decided by the coverage of the SiₓOᵧFz film. The RIE process parameters influencing SiₓOᵧFz film formation, coverage, removal and Si etching can be used to control the morphology of bSi. Two most important parameters for passivation film formation are O₂
concentration and the etching temperature. [37] Increasing the O₂ concentration enhances the deposition of SiₓOᵧFₓ film. [2] The SiₓOᵧFₓ film growth and integrity is susceptible to temperature variations. The film is unstable at higher temperatures and completely desorbs from the surface due to increase in temperature. [38] Also, the chances that the SiₓOᵧFₓ film will regrow on horizontal etched Si surface are minimum due to exothermic nature of Si etching. [23]

In a conventional RIE system, the temperature control is insufficient for the integrity of SiₓOᵧFₓ film and therefore RIE at cryogenic temperatures with efficient temperature control is more favourable. [39][38] High etch rate is desired from RIE tools operating at a cryogenic temperature which is achieved using two independent plasma sources. One source is inductively coupled plasma (ICP) source, which is responsible for creating high radical and ion density and the second is capacitively coupled plasma (CCP) source, which guides the ions from plasma towards substrate surface. [39] Two plasma sources allow independent control of the density of etching species and their energy. On the other hand, conventional RIE employs a single source, where etch rate increases with rf power at an expense of increased ion energies responsible for substrate damage and mask erosion. [39] Cryogenic RIE is superior for the formation and the stability of SiₓOᵧFₓ layer.

The SiₓOᵧFₓ etching heavily relies upon the ions being accelerated towards the target substrate. [40] Dual plasma source configuration offers independent control over the kinetic energy, density, and directionality of the ions and therefore allows more room for optimisation and etching of SiₓOᵧFₓ film. In combination, by employing a cryogenic dual source RIE system, one gains control over SiₓOᵧFₓ formation, removal, and Si etching and therefore topography and density of high aspect ratio micro and nanostructures. The configuration is typically known as ICP-RIE. Figure 3 shows the results of an ICP-RIE study using black silicon method. [39] In this study, bSi region was found as a function of temperature and oxygen content with fixed values of other parameters. The higher oxygen flows over-passivate the Si surface, whereas extremely low temperatures lead to SF₆ condensation. In both cases, etching is completely blocked. The solid line in Figure 3 represents the extreme etching anisotropy and the region above solid line is bSi region.
Figure 3. bSi fabrication in ICP-RIE as a function of O₂ content and temperature. [39]

The formation mechanism of bSi has been studied in detail and different models have been suggested for bSi formation mechanism. [40][41][42] In the beginning, the initial surface roughness of Si contributes to small scale structure formation. [42] The formation of initial surface roughness is attributed to either texturing by plasma ions or self-masking by Si₆O₇F₇ complexes. [43] The initial topography of the substrate plays an important role. The Si₆O₇F₇ layer formation and Si etching depend on the free diffusion of radicals to the substrate, and therefore the areas directly exposed to plasma are impacted more strongly than highly occluded areas. With initial surface structures on Si, Figure 4 shows a schematic of a model representing the circumstances for the evolution of bSi. [40] It can be seen that the Si₆O₇F₇ is thinner or absent at deep trenches or holes. The areas at top of the peaks have high exposure to plasma and are over passivated with Si₆O₇F₇, therefore the effective etching conditions are lower. The topographical saddle points shown in Figure 4 have balanced Si₆O₇F₇ formation and removal, and therefore the Si etching is higher compared to the peaks.

Figure 4. Evolution of bSi in ICP-RIE. The passivation layer formation and etching are dependent upon the geometry of the surface. The passivation layer growth at top of the peaks is faster, whereas it is minimum or zero at a high degree of occlusion. The areas without passivation lead to higher etch rate. The difference in etching leads to high aspect ratio structures. [40]

The process begins by initiation of a network of holes on Si surface with intrinsic surface roughness. The holes rapidly combine and form bigger holes and trenches. The difference in etching speeds between highly occluded holes/trenches and highly exposed peaks lead to deeper structures. Over time,
The planar areas are completely etched and needle-like bSi structures form. The results of the process are shown as a simulation and experimental observations in Figure 5. [40][41] It can be seen in Figure 5a, that with time the increase in aspect ratio slows down and the geometry evolves towards a configuration where the etch rate of holes and peaks balances. The simulation results and the experimental observations in Figure 4 are in close agreements with each other and therefore the results of this approach provide a good understanding of bSi evolution.

![Figure 5](image)

**Figure 5.** Evolution of bSi, a) Aspect ratio evolves with the time. Inset shows the formation of the holes in the beginning of the process and transformation into high aspect ratio bSi structures, b) Experimental results depict changes in Si surface area. Both the simulations and experimental observations are in close agreement. [41]

In addition to the pure SF$_6$/O$_2$ RIE chemistry, it is also possible to introduce reactive gases to the basic gas composition. Addition of methane (CH$_4$) to SF$_6$/O$_2$ can enhance polymer formation and high density pyramid like bSi can be achieved. [44] Typically, the etch rate of Si in Cl$_2$ RIE is lower compared to SF$_6$. Addition of Cl$_2$ to SF$_6$/O$_2$ is another alternative for bSi fabrication, which can broaden the gas composition window and enable removal of damage induced by RIE. [45]
Other gas chemistries can be employed in RIE to achieve bSi. Hydrogen bromide (HBr) and O₂ (HBr/O₂) mixture has been used for the fabrication of bSi.[46] In this process, Br is responsible for Si etching, whereas O₂ assists passivation. By careful adjustment of process parameters for etching and passivation, wide range of nanostructures can be achieved. Reactive gases such as silane (SiH₄), CH₄, argon (Ar), and hydrogen (H₂) can be employed to fabricate and control the morphology of structured surface. [47] SiH₄ and CH₄ plasma contribute to self-masking by forming silicon carbide (SiC), whereas Ar and H₂ plasma etch the unmasked areas. With this technique, bSi over a large area and with wide band absorption was demonstrated. [48]

Additional to conventional RIE techniques, several other configurations have been reported for the fabrication of bSi. Multi-cathode RIE system with high density plasma has been reported for the fabrication of bSi. [23] Plasma immersion ion implantation (PIII) with SF₆/O₂ gas chemistry is capable of producing bSi with a flexibility to control the shape and size of features. [49] Bosch process with its well-known alternating etching and passivation cycles can be adopted for the fabrication and optimisation of bSi, where repetition of cycles leads deep bSi structures with vertical sidewalls. [50]

RIE processes for bSi are commercially attractive due to superior technology integration and compatibility with other semiconductor processing. The fabrication of bSi can be integrated easily into a typical device fabrication. On the other hand, RIE process optimisation is rather complicated and improved skill set is needed for process improvement and development. Equipment cost is considered a major drawback but can be compensated with batch processing and large throughput.

2.3 Material properties

Black silicon as a material possesses many attractive properties. However, in this section, only the properties of bSi relevant to the focus of this thesis are introduced and discussed. The focus of the research work performed in this thesis was optimisation of bSi for optical, wetting and de-wetting enhancement. In the beginning, optical behaviour of bSi fabricated by ICP-RIE from UV to mid-IR is discussed. Along with the optical properties, a brief introduction to the plasmonic behaviour of bSi is also presented. Later, an introduction to the wetting behaviour of different surfaces along with the transition of wetting characteristics into different wetting regimes is highlighted.

Optical properties

The nanostructured bSi surface exhibits exceptionally good anti-reflection properties in the visible spectrum and also a strong light trapping in near-infrared (NIR), shown in Figure 6a. The reduced reflectance by bSi is due to different reasons, which are dependent on the size and shape of bSi features. The interaction of light and bSi could vary depending on the geometry of the
Typically, for a structured surface, the reduced reflection is observed due to pronounced interaction of light with the highly topographical surface. Taking into consideration the roughness, the anti-reflection behaviour can be explained in different ways.

Firstly, when the roughness features are very small (sub 100 nm), the correlation length \( L_c \) is much smaller than the scaled wavelength \( \lambda/n_{Si} \) (\( \lambda \) is the wavelength and \( n_{Si} \) is the refractive index of Si) of incoming light and the effective medium theory is applicable. In an effective medium, the incoming wavelengths do not resolve very small features. A smooth transition of refractive index from air to bulk Si through effective medium leads to graded refractive index. The gradual transition of refractive index from air to Si composes an effective anti-reflection coating on the surface.

Secondly, when the size of roughness features is much larger compared to the incoming wavelength or more precisely \( L_c \) is larger than the scaled wavelength, the anti-reflection behaviour can be explained by geometric optics as multiple interactions of rays of light until they are lost.

Thirdly, when \( L_c \) is neither too small nor too large and is in the order of scaled wavelength. Both, refractive index theory and geometric optics are not able to provide reliable quantitative scale of bSi features. Figure 6 shows the measured and calculated optical spectra of two such bSi samples. Sample A contains deeper and steeper features than sample B and therefore causes the difference in reflectance, which will be discussed later. As shown in Figure 6a, the total reflectance of bSi is very small compared to the polished Si wafer but still higher than a theoretical calculated anti-reflection coating.

![Figure 6. Optical spectra of bSi a-c) Reflectance, absorption and transmission of two different bSi samples and a calculated perfect ARC coating. bSi samples are have very low reflectance from UV-NIR b) Component of diffuse reflectance inside the measured reflectance. [51] [Reprinted according to the guidelines provided by SPIE]

Figure 6d shows the contribution of diffuse reflectance in overall reflectance of bSi. It can be seen that most of the reflected light in UV and visible is scattered. This is an indication that light distinctly interacts with bSi features.
and bSi does not behave like effective medium at those wavelengths. Scattering decreases with increasing wavelength at NIR and sample B with less steep bSi profile sees a dramatic drop in scattering. Scattering increases for a short wavelength range above 1000 nm and at further higher wavelengths, the scattering finds a decreasing trend.

The NIR trapping shown in Figure 6b and Figure 6c highlights that some scattering into larger angles occurs and therefore even stronger scattering can be expected at smaller wavelengths. [43] In order to elaborate the observed optical behaviour of bSi, a deeper understanding of bSi interaction with light and influence of its structural topography is required. Figure 7 shows results of a study where optical responses of different bSi topographies were studied and recorded by FDTD simulations and experiments. [43] In the simulations, a numerical model was constructed by extracting roughness peaks and trenches from a SEM image of the bSi sample, shown in Figure 7a. The geometric parameters were varied by scaling the basic structure.

![Figure 7](image)

**Figure 7.** Optical and morphological properties of bSi. a-d) Simulation results showing the extracted model and reflectance of bSi with different Lc and two different feature depths (H).

Figure 7b shows the influence of Lc and H on light trapping efficiency. The light trapping efficiency increases with increasing Lc. Features with low H see higher trend for light trapping with increasing Lc. At higher Lc, the light trapping efficiency saturates and becomes equal for different H. Reflectance spectra shown in Figure 7 (c, d) show that the reflectance increases with Lc and strongly decreases with increase in H.

The experimental results with variation in geometrical parameters are highlighted in Figure 8. As shown in Figure 8a, the overall reflectance decreases with increased etch duration. As shown in Figure 8b, Lc and H
increase with etching time. This influence can be described by consideration of spatial frequency of bSi features, mediating coupling of incoming light into different scattering angles. When $L_c$ is low, the surface contains high spatial frequencies that couple the incoming light to the evanescent waves, which do not propagate. On the other hand, higher $L_c$ leads to narrow spatial frequency distributions, with stronger coupling. The scattered waves will also couple back to low propagation angles with increasing propagation length. The larger structures with low spatial frequency component couple the incident light into backscattered waves and reflect more light. However, if the bSi structures are deep and have steep sidewalls the backscattering is very low and result in an extremely reduced overall reflectance. This behaviour explains the different optical response of bSi with different surface topographies.

![Figure 8](image)

**Figure 8.** Influence etching duration on geometry and optical response, a) reflectance increases with increases of etch duration, b) $L_c$ and $H$, as a function of etch duration. [43]

The geometrical parameters of bSi surface structures play an important role in trapping the incoming light of a wide spectrum. The efficient light trapping behaviour of bSi has been combined with metals (Ag and Au) to convert the trapped photons into plasmons. [52][53][54] On such roughened surface, surface plasmon resonance (SPR) greatly amplifies a Raman signal and geometry of the metal surface, optical constant and surroundings play an important role. [52] The enhancement effect at the surface is overwhelming compared to the bulk and therefore the technique is known as surface-enhanced Raman spectroscopy (SERS). Two primary enhancement mechanisms are electromagnetic (EM) and chemical. [55] The enhancement on a roughened surface is a direct consequence of EM mechanism which strongly depends on the size of metallic nanostructures. Due to the small size of metallic nanostructures, localised surface plasmons excite and produce EM energy density around the nanostructures. [56] This energy density is a major contributor towards the dominant EM enhancement mechanism and ultimately SERS. [57]

SERS is a well-established and a powerful analysis technique, where an optimised SERS substrate (template) is used to analyse different chemical species. [58] In order to perform such analysis, a chemical analyte is adsorbed onto or placed on a SERS substrate. Next, Raman spectra are recorded from the substrate. Vibrations in chemical bonds of the analyte can induce a shift in Raman signal. This shift corresponds to a specific chemical bonding or
composition and is therefore used to identify most chemical species. [59] Ultra-sensitivity of SERS substrates enables molecular recognition of target analyte even in an extremely low concentration. SERS can be achieved and maximised by a careful optimisation of SERS substrate and also by improving the adsorption of analytes. [58]

Sensitivity of a SERS substrate known as enhancement factor is estimated with the help of a sensing molecule. Rhodamine 6G (R6G) has been known for an active role in SERS as it is one of the first sensing molecule used for single molecule SERS, where high enhancement factors have been reported. [60] However, R6G possesses large molecular cross-section and a Raman cross-section, which is not considered as a typical Raman cross-section. [61] The large Raman cross-section leads to an intense SERS spectrum. Raman cross-section of R6G’s most intense band at 532nm excitation is extraordinarily intense than various other molecules. [62] It has also been reported that the molecular cross-section of R6G molecule changes on a metal surface and formation of R6G dimer aggregates even in low concentrations contributes to a complex spectral coupling. [63] The large enhancement factor estimated from R6G molecule does not constitute a general enhancement factor.

Wetting properties

The wetting behaviour of solid surface towards a liquid droplet in a fluid medium is expressed as a contact angle (CA). For a smooth, chemically and physically homogeneous solid surface in thermodynamic equilibrium, CA is the angle of contact between liquid droplet and the solid surface. [64] Under these circumstances, the CA can be determined by Young’s formula: [65]

\[ \gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta_e \]  

In equation 1, \( \gamma_{SV} \), \( \gamma_{SL} \) and \( \gamma_{LV} \) are the interface free energies of solid-vapour, solid-liquid and liquid-vapour, respectively, and \( \theta_e \) is the equilibrium CA or Young’s CA (\( \theta_Y \)).

The wetting behaviour of a smooth surface is shown in Figure 9, where surface properties are determined using CA. [65] The surface with CA > 90° shows reduced wetting (Figure 9a) and therefore termed as hydrophobic surface, whereas CA < 90° results in increased wetting (Figure 9b) and are called hydrophilic surface. In the case of complete wetting, the surfaces are called superhydrophilic (Figure 9c). For CA > 150°, the surface is called superhydrophobic.

![Figure 9](image)
In practice, two types of CA measurements are used to characterise the surfaces, i.e. static CA and dynamic CA. [66] For a smooth homogeneous surface, measured static CA is close to equilibrium CA whereas dynamic CA is a non-equilibrium CA. Static CA is measured using sessile drop method by placing a droplet and recording it with a goniometer. Dynamic CA measurements are performed by increasing (advancing CA) and decreasing (receding CA) the droplet volume. The difference between advancing and receding CAs is called contact angle hysteresis.

The nanostructured bSi surface is non-homogenous and contains periodic roughness. In the case of rough surfaces like bSi, the liquid droplet either penetrates the structures or stays suspended on top with air trapped underneath, shown in Figure 10. In either case, the CA is enhanced and the above explained Young’s equation is not directly applicable. The penetration scenario depicted in Figure 10a is based on Wenzel model. [67] Whereas, the suspension of droplet shown in Figure 10b is based on Cassie-Baxter model. The CA on rough surfaces is referred to as apparent CA.

In Wenzel model, the liquid follows the surface topography (Figure 10a) and in a thermodynamic equilibrium there exists a linear relationship between the apparent CA ($\theta^a$) and the roughness factor ($r$), defined as:

$$
\cos \theta^a = r \cos \theta_f
$$

(2)

The roughness factor is a ratio of the true area of roughened surface and its projection. Based on Wenzel model, the introduction of roughness to intrinsically hydrophilic surface enhances hydrophilicity, whereas the hydrophobic surface with roughness gains hydrophobicity. For a hydrophobic surface in Wenzel model, apparent CA and CA hysteresis increases with increased roughness factor. At very high roughness factor, the CA hysteresis starts to decrease due to increased air fraction between the roughness features. The Wenzel’s prediction breaks down and the liquid droplet assumes Cassie-Baxter state or composite state, shown in Figure 10b. [68]

![Figure 10](Publication 2)

**Figure 10.** Water droplet behaviour on the rough surface a) droplet penetrating into structures with no air trapped underneath, Wenzel state, b) droplet suspended on top of structures with air trapped underneath, Cassie-Baxter state. (Publication 2)

In the Cassie-Baxter model with periodic structures like bSi, the apparent CA ($\theta^a$) can be calculated by using the equation 3: [66]

$$
\cos \theta^a = f (1 + \cos \theta_f) - 1
$$

(3)
In equation 3, \( f \) is the fraction of the solid in contact with the liquid droplet. To achieve the Cassie-Baxter state, a solid material with large CA and the least contribution of solid part with the droplet is necessary.

The bare bSi and polished Si surface after exposure in the air are similar, i.e. contains a thin layer of native oxide. Oxidised Si is hydrophilic and therefore the introduction of roughness, i.e. bSi, makes it more hydrophilic. [67] The hydrophilicity of bSi follows the Wenzel model. On the other hand, deposition of low surface energy materials on bSi forms a roughened hydrophobic surface. [66] Such bSi shows high apparent CA and very low hysteresis, which means low surface energy coated bSi follows Cassie-Baxter model.

2.4 Uses

As a material, bSi produced by ICP-RIE with SF\(_6\) and O\(_2\) chemistry is essentially the same as planar Si. However, the periodic roughness of bSi enables many attractive properties, which are either lacking in Si or are superior to Si. The role of bSi structures for optical and wetting properties has been discussed above. Extremely low reflectance, larger wetting/non-wetting regime, and nanostructured surface with a large chemically active surface area are responsible for a plethora of applications.[23] Furthermore, the integration of other material to bSi enable properties which are otherwise absent in Si.

Improved light trapping and anti-reflection properties of bSi are very attractive for solar cells. [69][70] The efficient light management of bSi has been used to demonstrate solar cells with improved cell efficiency. [71] Enhanced absorption and sensitivity of bSi in a wide spectrum have been beneficial for the development of efficient photodetectors. [72][73][74] Using bSi, large area SERS substrate for gas sensing applications has been demonstrated. [59] bSi based SERS templates for ultrasensitive molecular detections are also commercially available. [75]

The surface structures of bSi facilitate fabrication of wetting/non-wetting regimes on a Si substrate. Superhydrophobic and superhydrophilic surfaces have been demonstrated using bSi with different surface modification techniques. [76] These surfaces possess anti-sticking, anti-contamination, self-cleaning properties which are beneficial for industrial and biological applications such as anti-biofouling for boats, anti-sticking of snow for antennas and windows, anti-fogging, self-cleaning and stain resistant surfaces. [66]

Large surface area of bSi is optimum for a wide variety of chemical and physical reactions. The intrinsic morphology of bSi has been employed for chemical and biological sensors.[77] The surface nanostructures of bSi have been used in advanced assembly techniques for BioMEMS applications. [78] The bSi has been used as a support platform for mass spectrometry. [79] High aspect ratio bSi have shown bactericidal activity.[80] Furthermore, bSi has shown promises for smart packaging, fluidic interconnects for microsystems, electronic assembly, and hybrid polymer-ceramic silicon systems. [81][82]
Black silicon
3. Experimental techniques

In order to fabricate and integrate bSi to targeted applications, a wide range of materials and processing techniques were investigated and applied in this work. This section provides a brief overview of the employed fabrication and characterization methods.

3.1 Deposition

In publications 1-4, plasma enhanced chemical vapour deposition (PECVD) was used to deposit SiO₂ mask material to achieve patterned bSi. Oxford Instruments Plasmalab80Plus parallel plate reactor with heated and grounded substrate electrode was used. Silane (SiH₄) and nitrous oxide (N₂O) were used to deposit SiO₂ (Figure 11a).[83] The deposition was performed on a 100 mm wafer at 300 °C, 1000 mtorr and 20 W forward power. The measured deposition rate was of 65nm/min over a 100 mm wafer.

![Figure 11. Oxford Instruments Plasmalab80plus a) PECVD, b) RIE system.][83]

For publications 1-4, fluoropolymer deposition on bSi was performed in an RIE system. Oxford Instruments Plasmalab80Plus parallel plate reactor with water cooled and biased substrate electrode was used. Trifluoromethane (CHF₃) gas precursor was used to deposit the fluoropolymer (Figure 11b). [83] The deposition was carried out on a 100 mm wafer at room temperature, 250 mtorr, 250 W power and 50 sccm CHF₃. The deposition rate was 8 nm/min.

In publication 6, bSi was coated with pyrolytic carbon (PyC). The deposition was performed by using a hot wall chemical vapour deposition (CVD).[84] The system employs methane/hydrogen mixture as a carbon source and is equipped with a cylindrical quartz chamber, a tubular furnace, a computer...
controlled vacuum pump and gas flow controllers. The thickness of the fabricated PyC films is determined by the methane concentration in the hydrogen-methane gas mixture and pressure in the CVD chamber. The dependence of the deposited PyC film thickness on methane concentration has been experimentally demonstrated. [85] The deposited thickness was 20-30 nm.

In publication 5, parylene polymer was deposited on bSi in an SCS Labcoter 2 (PDS 2010) vapour deposition system. [86] The parylene deposition process consists of three steps, i.e. vaporization, pyrolysis, and deposition. In the vaporization step, the solid dimer is vaporized in a furnace at 150 °C. In pyrolysis step, the vaporised dimer is brought to the pyrolysis chamber and quantitatively cleaved at 680 °C to form monomers. In the last step, the monomer enters the deposition chamber and deposits on target substrate maintained at room temperature. The parylene polymer chosen for this work was poly-monochloro-p-xylylene (parylene-C) and the deposited thickness was 250 nm.

In publication 7, bSi was coated with titanium(Ti) and silver(Ag) in a Instrumentti Mattila Oy e-beam evaporator (IM-9912). Thin Ti film (4 nm) was evaporated at 0.01 nm/sec and used as an adhesion layer. Different thicknesses of Ag ranging from 35 to 150 nm were deposited at a deposition rate of 0.35 nm/s.

3.2 Patterning

The pattern design was performed in CleWin 4 layout editor. [87] The design file was used to fabricate photolithography masks on a 125 mm × 125 mm glass templates containing low reflective chromium and AZ1518 photoresist layer. [88] The designed patterns were transferred to AZ1518 photoresist in Microtech LW 405 LaserWriter. [89] For low-resolution masks, spot size of 8 μm was used whereas high-resolution patterns were written with a spot size of 2 μm. The exposed masks were developed in AZ351 developer. Chromium etching was performed in a chromium etchant mixture composed of ceric ammonium nitrate and nitric acid. [90] Photoresist was removed using acetone in a spin dryer followed by rinsing with isopropanol. In the final step, the mask template was cleaned in a piranha solution (HNO₃:H₂O₂, 1:3) and rinsed with deionized (DI) water.

In publications 1-4, the pattern definition was performed using photolithography. The image reversal photoresist AZ5214E was used.[91] An oxidised Si wafer was spin coated (4000 rpm) by AZ5214E for 1 min followed by pre-baking at 95.5 °C. Next, the coated wafer was exposed to UV through a glass mask using a Carl-Sus MA-6 mask aligner.[92] The post-exposure development was performed in AZ351 developer. After inspection with an optical microscope, the successful wafer was hard baked at 120 °C. For image reversal process, a post-bake step after first UV exposure followed by flood exposure was introduced before the development. The measured thickness of
Experimental techniques

the resist with this process was 1.44 μm. The photolithography steps adopted in this work are depicted in Figure 12.

Figure 12. Photolithography a) oxidised Si substrate, b) spin coating of photoresist and prebaking, c) UV exposure through a glass mask with desired patterns, d) development and post-baking.

In publication 5, environmental scanning electron microscope (ESEM) was used for direct patterning of extreme wetting contrast. The patterns were generated in Carl Zeiss EVO HD-15-LS ESEM in the presence of water vapour. In this process, the electron beam generates a localised plasma by ionizing water vapour and nitrogen in the chamber. The interaction of localised plasma with the substrate modifies the wetting locally and the changes proceed with the scanning of the electron beam. The local electron beam exposure was performed at working distance of 4.5 mm, chamber pressure of 4.5 Torr, the acceleration voltage of 30 kV, beam current of 5 nA and an exposure dose of 2.5 mC/cm². The schematic of the patterning process is shown in Figure 13.

Figure 13. Direct pattern writing in ESEM. The localised electron beam creates a plasma where the plasma species reacts with the bSi coated with fluoropolymer locally and change the wetting behaviour. The treated area in the inset on the left shows surface turning into superhydrophilic, whereas the untreated area stays superhydrophobic. (Publication 5)

3.3 Etching

In publication 1-4, SiO₂ was patterned using dry etching with a photoresist mask. The etching was performed in Oxford Instruments Plasmalab80Plus parallel plate RIE with water cooled graphite biased substrate electrode (Figure 11b).[93] To etch SiO₂, CHF₃ (25 sccm) and Ar (5 sccm) gas etch chemistry was used at a process pressure of 30 mtorr and forward power of
250 W. The recorded etch rate for a 100 mm wafer with 85 %- 90 % exposed area of SiO₂ was 35 nm/min). The fluorination of parylene-C film (Publication 5) was also performed in the same tool for 1 min with SF₆ flow of 100 sccm, the forward power of 100 W and 20 mtorr pressure. The fluorination reduced the thickness of parylene-C by 100 nm. Photoresist removal after SiO₂ dry etching was done in Oxford Instruments Plasma Stripper PRS900 in oxygen plasma ambient.

The fabrication of bSi was performed in Oxford Instruments Plasmalab System 100-ICP180, shown in Figure 14. [94] The tool is equipped with a double plasma source, i.e. ICP and CCP, and therefore allows independent control over density and directionality of ions. The sample table is cooled to cryogenic temperatures with liquid N₂ and the heat transfer is ensured by helium backside cooling. The high-density plasma is created in alumina dome and the wafer is mechanically clamped by alumina clamp. The operating pressures and temperatures are up to 100 mTorr and -150 °C to 400 °C, respectively.

Figure 14. Plasmalab System100-ICP180 a) the process chamber. ICP (above) breaks down etching gases in alumina dome and generates ions and radicals. Ions are accelerated by CCP toward the substrate. The substrate clamped from above rests on cryogenically cooled aluminium chuck. He backside cooling ensures the temperature uniformity, b) Picture of the tool with a load lock. [94]

The SF₆ and O₂ gas chemistry combination was used for bSi formation. In publication 1, the effect of process parameters on bSi was studied. For the applications presented in publications 2-7, two types of bSi substrates were fabricated. Tall spikes were fabricated using ICP 1000 W, CCP 6 W, the pressure of 10 mtorr, SF₆ flow of 40 sccm, O₂ flow of 18 sccm, the temperature of -110 °C with 7 minutes of temperature stabilization and followed by 7 minutes of etching. For smaller bSi structures, SF₆ flow of 30.5 sccm, O₂ flow of 27.5 sccm and CCP power of 4 W was used.

In publications 3-4, wet etching of SiO₂ was performed in buffered hydrofluoric acid (BHF) solution at 30 °C. BHF is composed of ammonium fluoride and hydrofluoric acid based etching mixture. [95] The etch rate of thermal oxide is 120 nm/min. In this work, PECVD SiO₂ has been used and the observed etch rate was 3-4 order of magnitude higher than thermal oxide, which has been observed in other studies. [96]
3.4 Characterization

A variety of techniques was used to characterise the fabrication and properties of bSi. The film thicknesses were measured with a PLASMOS SD 2300 ellipsometer using rotating analyser and helium-neon (He-Ne) laser at 70° incidence as a light source. [97] Average step height of patterned profile was recorded at different stages of fabrication using Bruker Dektak XT surface profilometer. [98] The surface morphology and cross-sectional profile of bSi and fabricated patterns were imaged in a Zeiss Supra 40 field emission (FE) scanning electron microscope (SEM). [99]

Wetting behaviour was measured and analysed with the help of a contact angle meter Attention Theta by Biolin Scientific. [100] Static contact angle measurement was performed by placing a sessile droplet on the solid substrate. The software recorded the image of the droplet and defined the static contact angle by fitting the Young-Laplace equation around the droplet. Dynamic contact angles were measured by volume changing method. A small droplet was first placed on the surface. The needle was brought closer to the substrate and the volume of the droplet was increased while recording the advancing contact angle. For receding contact angle, the droplet volume was gradually decreased.

The reflectance measurements were carried out using Perkin Elmer Lambda 950 UV-Vis-NIR spectrometer with 150 mm integrating sphere. [101] Total reflectance was measured by placing the sample at the back of the integrating sphere. Incoming light with an angle of incidence of 6°-8° was reflected back of the sample and collected by the sphere. The optical reflectance spectra were obtained in the region of 220 nm-2000 nm with a wavelength step of 2nm. Baseline spectrum was measured with a white standard mirror plate instead of a sample placed at the back of the integrating sphere. During the measurements, the same mirror was placed behind the sample.

The self-assembly tests were carried out using a hybrid microassembly platform. [102][103] The platform consists of a custom designed microgripper, four motorized stages, a water droplet dispenser, an adhesive dispenser, an ultrasonic humidifier, two microscopes connected to two video cameras and a high-speed camera. The microgripper was used to place the microchips near or on top of the receptor site. The motorized stages were responsible for moving the microgripper (z-axis) and the sample carrier (x, y and z-axis). Water and adhesive droplets were delivered to receptor site or the whole wafer by dedicated dispensers. The microscopic droplets were produced by the ultrasonic humidifier. Two microscopes, one on the top and one to the side were installed to observe the assembly process. The high-speed camera was used to record the deposition of microscopic droplets.

The sample inspection was routinely performed in white light optical microscopes. Raman measurements were performed using Witec Alpha 300R confocal Raman microscope. [104] X-ray photoelectron spectroscopy (XPS) measurements were done using Kratos Analytical AXIS Ultra. [105] Surface topography of parylene-C coated bSi was carried out using Dimension 5000 (Veeco) atomic force microscope (AFM).
Experimental techniques
4. Results and applications

In the beginning of this chapter, details and the influences of process parameters on bSi formation are introduced. Furthermore, the relationship of process parameters for different types of bSi is evaluated. Finally, the integration of bSi for potential applications is discussed.

4.1 Fabrication of bSi

The nanostructured bSi is achieved by optimising several processing parameters in ICP-RIE. To evaluate the influence of all these parameters requires an extensive amount of experiments, which is time and cost consuming. The design of experiments (DOE) using Taguchi method is known to reduce the number of experiments to a practical level. The method has well-defined guidelines and uses a special set of arrays called orthogonal arrays. These standard arrays specify a protocol to extract information of all the influencing factors by employing a minimal number of experiments. Different studies reported DOE with Taguchi for studying the influence of process parameters in plasma etching and machining techniques. [106][107]

In order to experimentally investigate the formation of bSi, DOE using Taguchi method was employed in publication 1. The DOE steps are as follows: (a) problem identification and definition of objectives; (b) quality characteristics, factors, levels and interactions; (c) experimental design using orthogonal arrays; (d) experiments; (e) analysis; (f) confirmation runs. The Taguchi DOE process steps are shown in Figure 15.

![Figure 15. DOE using Taguchi method. [106]](image)

The main objective of research work in publication 1 was to study and optimise the bSi process by conducting fewer experiments. As shown in Figure 16, height (h), width (w) of bSi spike and the amount Si etched (t) were considered measured quality characteristics. Temperature, capacitively
coupled plasma (CCP) power, SF$_6$/O$_2$ gas flows and pressure were chosen factors (variable parameters). These parameters have a strong influence on passivation layer formation and removal and therefore contribute strongly to bSi formation. Lower temperatures and higher oxygen flows contribute to the thicker passivation layer, whereas, higher CCP results in more energetic ion bombardment leading to increased passivation removal. The chamber pressure controls the directionality of the ions, and therefore nature (anisotropic/isotropic) of the passivation removal.

![Diagram](Figure 16. Width (w), height (h) and etched Si (t) as measured quality characteristics of bSi. The measurement was performed with the help of a SEM. (Publication 1)

Three different factor levels were used. As shown in Table 1, each level is composed of a different parameter set. With three different levels of four factors, L$_9$ orthogonal array shown in Table 2 is suitable for understanding the influence of those factors. The number of experiments is reduced from $81 (3^4)$ to 9. The vertical column under each factor contains levels appearing in an equal number of times and the described sequence of experiments is maintained to ensure that factor columns are mutually orthogonal. Experiment 1 is repeated twice to check the repeatability of the process.

### Table 1. Three different levels used in DOE. Each level is composed of a unique set of parameters.

<table>
<thead>
<tr>
<th>Levels</th>
<th>Pressure (mTorr)</th>
<th>CCP Power (W)</th>
<th>SF$_6$/O$_2$ flow (sccm)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Level 1</td>
<td>10</td>
<td>2</td>
<td>40/18</td>
<td>-140</td>
</tr>
<tr>
<td>Level 2</td>
<td>20</td>
<td>4</td>
<td>30.5/27.5</td>
<td>-110</td>
</tr>
<tr>
<td>Level 3</td>
<td>30</td>
<td>6</td>
<td>47/11</td>
<td>-80</td>
</tr>
</tbody>
</table>

### Table 2. An experimental design using L$_9$ Orthogonal arrays. Experiment # 1 was repeated twice to evaluate the repeatability.

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>Pressure (mTorr)</th>
<th>CCP Power (W)</th>
<th>SF$_6$/O$_2$ flow (sccm)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Level 1</td>
<td>Level 1</td>
<td>Level 1</td>
<td>Level 1</td>
</tr>
<tr>
<td>2</td>
<td>Level 1</td>
<td>Level 2</td>
<td>Level 2</td>
<td>Level 2</td>
</tr>
<tr>
<td>3</td>
<td>Level 1</td>
<td>Level 3</td>
<td>Level 3</td>
<td>Level 3</td>
</tr>
<tr>
<td>4</td>
<td>Level 2</td>
<td>Level 1</td>
<td>Level 2</td>
<td>Level 3</td>
</tr>
<tr>
<td>5</td>
<td>Level 2</td>
<td>Level 2</td>
<td>Level 3</td>
<td>Level 1</td>
</tr>
<tr>
<td>#1 Repeat</td>
<td>Level 1</td>
<td>Level 1</td>
<td>Level 1</td>
<td>Level 1</td>
</tr>
<tr>
<td>6</td>
<td>Level 2</td>
<td>Level 3</td>
<td>Level 1</td>
<td>Level 2</td>
</tr>
<tr>
<td>7</td>
<td>Level 3</td>
<td>Level 1</td>
<td>Level 3</td>
<td>Level 2</td>
</tr>
<tr>
<td>8</td>
<td>Level 3</td>
<td>Level 2</td>
<td>Level 1</td>
<td>Level 3</td>
</tr>
<tr>
<td>9</td>
<td>Level 3</td>
<td>Level 3</td>
<td>Level 2</td>
<td>Level 1</td>
</tr>
<tr>
<td>#1 Repeat2</td>
<td>Level 1</td>
<td>Level 1</td>
<td>Level 1</td>
<td>Level 1</td>
</tr>
</tbody>
</table>

The ICP power was fixed at 1kW. The etch process was constructed by using 5 minutes of temperature stabilization and 7 minutes of etching. The wafer was clamped to the cooled electrode and helium backside pressure was maintained.
to ensure efficient heat exchange between the substrate and the cooled electrode. Eleven identical wafers were prepared by patterning SiO₂ in RIE using photolithographically defined photoresist mask. The photoresist mask was removed and all the wafers were etched in ICP-RIE using the sequence of experiments shown in Table 2. The values of \( h, w, \) and \( t \) were measured using scanning electron microscope and the average measurement results are computed in Table 3.

**Table 3.** Measurement of width (w), height (h) and etched Si (t) using scanning electron microscope.

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>h (( \mu )m)</th>
<th>w (( \mu )m)</th>
<th>t (( \mu )m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.31</td>
<td>0.2</td>
<td>1.48</td>
</tr>
<tr>
<td>2</td>
<td>0.45</td>
<td>0.2</td>
<td>1.0</td>
</tr>
<tr>
<td>3</td>
<td>0.0</td>
<td>0.0</td>
<td>15.6</td>
</tr>
<tr>
<td>4</td>
<td>0.60</td>
<td>0.79</td>
<td>0.99</td>
</tr>
<tr>
<td>5</td>
<td>2.85</td>
<td>0.57</td>
<td>2.99</td>
</tr>
<tr>
<td>#1 Repeat1</td>
<td>0.41</td>
<td>0.23</td>
<td>2.02</td>
</tr>
<tr>
<td>6</td>
<td>1.45</td>
<td>1.02</td>
<td>0.96</td>
</tr>
<tr>
<td>7</td>
<td>1.97</td>
<td>0.78</td>
<td>0.49</td>
</tr>
<tr>
<td>8</td>
<td>6.83</td>
<td>5.0</td>
<td>0.57</td>
</tr>
<tr>
<td>9</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>#1 Repeat2</td>
<td>0.23</td>
<td>0.18</td>
<td>1.64</td>
</tr>
</tbody>
</table>

In order to analyse the experimental results, the influence of each factor on height, width and etched Si, the mean values for each level were calculated and computed in Table 4. The difference between highest and lowest parameter value (delta) was used to determine the influential rank. The rank value varies from 1-4, with 1 originating from the highest delta value and having the strongest influence compared to other factors.

**Table 4.** Mean and influential rank of four factors for height, width of bSi and the etched Si.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Levels</th>
<th>Pressure</th>
<th>CCP Power</th>
<th>SF(_6)/O(_2)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>h (( \mu )m)</td>
<td>Level 1</td>
<td>0.25</td>
<td>0.96</td>
<td>2.86</td>
<td>1.05</td>
</tr>
<tr>
<td></td>
<td>Level 2</td>
<td>1.63</td>
<td>3.38</td>
<td>0.35</td>
<td>1.29</td>
</tr>
<tr>
<td></td>
<td>Level 3</td>
<td>2.93</td>
<td>0.48</td>
<td>1.61</td>
<td>2.48</td>
</tr>
<tr>
<td></td>
<td>Delta</td>
<td>2.68</td>
<td>2.89</td>
<td>1.26</td>
<td>1.42</td>
</tr>
<tr>
<td></td>
<td>Rank</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>w (( \mu )m)</td>
<td>Level 1</td>
<td>0.13</td>
<td>0.59</td>
<td>2.07</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>Level 2</td>
<td>0.79</td>
<td>1.92</td>
<td>0.33</td>
<td>0.67</td>
</tr>
<tr>
<td></td>
<td>Level 3</td>
<td>1.93</td>
<td>0.34</td>
<td>0.45</td>
<td>1.93</td>
</tr>
<tr>
<td></td>
<td>Delta</td>
<td>1.79</td>
<td>1.58</td>
<td>1.74</td>
<td>1.67</td>
</tr>
<tr>
<td></td>
<td>Rank</td>
<td>1</td>
<td>4</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>t (( \mu )m)</td>
<td>Level 1</td>
<td>6.03</td>
<td>0.99</td>
<td>1.00</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>Level 2</td>
<td>1.41</td>
<td>1.29</td>
<td>0.66</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>Level 3</td>
<td>0.35</td>
<td>5.52</td>
<td>6.13</td>
<td>5.72</td>
</tr>
<tr>
<td></td>
<td>Delta</td>
<td>5.67</td>
<td>4.53</td>
<td>5.46</td>
<td>4.90</td>
</tr>
<tr>
<td></td>
<td>Rank</td>
<td>1</td>
<td>4</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>

The rank values calculated in Table 4 show the influence of each factor for measured parameter. It can be seen that for the height of bSi, the rank of CCP > pressure > SF\(_6\)/O\(_2\) > temperature. For the width of bSi and the etched Si, the rank of pressure > SF\(_6\)/O\(_2\) > temperature > CCP. The relationship between the four factors and the measured parameters is depicted in trend charts, shown in Figure 17. From the Figure 17, it can be seen that the bSi formation is favoured at higher pressures, intermediate CCP power, intermediate SF\(_6\)/O\(_2\) ratio, and higher temperatures. Also, Si etching is significantly higher at lower pressures, higher SF\(_6\)/O\(_2\) ratio, higher CCP power, and higher temperatures.
Results and applications

Figure 17. Trend charts of four parameters versus the measured parameters. The x-axis represents four sub axis of factors. Y-axis shows the width (w), height (h) and Si (t) in micrometres. (Publication 1)

At low pressures, the directionality of ions ensures directional and efficient removal of passivation from the horizontal surface and therefore the bSi formation is less pronounced and Si etching is higher. At higher pressures, the passivation removal is less directional. The self-passivation and etching regime is promoted, where Si etching is reduced and bSi formation is enhanced.

The CCP power determines the energy of the ions that are responsible for removal the passivation by sputtering. At lower CCP powers, the ions do not possess the significant energy to remove the passivation. The Si etching is blocked and therefore bSi formation is hindered. On the other hand, too high CCP power completely removes the passivation layer and bSi formation is inhibited by significant bulk Si etching. At intermediate CCP, bSi is produced and as shown in Table 4, the influence of CCP is strongest for the height of the spikes.

As seen from Figure 17, the gas flow ratio (SF₆/O₂) ratio has a similar trend as CCP power. At lower ratios (higher O₂ content), the passivation layer is strong. The over-passivation regime blocks the Si etching and therefore bSi cannot form. At higher ratio (lower O₂ content), the passivation layer is weak. The higher SF₆ content etches bulk Si and therefore bSi formation is blocked. An intermediate ratio of SF₆ and O₂ is necessary for bSi formation. The passivation layer is sensitive to temperature variations and is more stable at lower temperatures. Poor stability of the passivation film at higher temperatures leads to higher Si etching.

Other than the measured parameters, the factors also influenced the shape and sidewall profile of the bSi structures. Decrease in pressure lead to sharp, dense and vertical spikes, whereas an increase in pressure produced less dense spikes with positive slopes. Higher CCP also produced bSi structures with positive slopes. Based on the measurement results and bSi profile observations from Table 4 and Figure 17, the process parameters were optimised and four different bSi topographies were fabricated. Table 5 shows the parameters used for bSi Type1-Type4 and the recorded SEM images are shown in Figure 18. For the fabrication of these four types, unmasked Si wafers were used. The parameter values other than mentioned in Table 5 were kept the same as initial DOE.
Table 5. Parameter values for four different types of bSi fabricated.

<table>
<thead>
<tr>
<th>Type</th>
<th>Pressure (mTorr)</th>
<th>CCP Power (W)</th>
<th>SF&lt;sub&gt;6&lt;/sub&gt;/O&lt;sub&gt;2&lt;/sub&gt; flow (sccm)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 1</td>
<td>10</td>
<td>3</td>
<td>47/11</td>
<td>-120</td>
</tr>
<tr>
<td>Type 2</td>
<td>20</td>
<td>6</td>
<td>40/18</td>
<td>-110</td>
</tr>
<tr>
<td>Type 3</td>
<td>10</td>
<td>2</td>
<td>40/18</td>
<td>-120</td>
</tr>
<tr>
<td>Type 4</td>
<td>10</td>
<td>2</td>
<td>20/18</td>
<td>-120</td>
</tr>
</tbody>
</table>

Figure 18. Four types of fabricated bSi. Type 1 is composed of dense, high aspect ratio spikes with vertical sidewalls. Type 2 is a smooth sidewall and pyramid-like positively tapered bSi. Type 3 has smaller features compared to type 1 and type 2 and the high aspect ratio features are slightly positively tapered, Type 4 contains the smallest features and the wafer surface looks rather brownish with the naked eye. (Publication 1)

The repeatability of the experiments was evaluated by running the experiment number 1 twice after the first execution. The samples were inspected along with other experiments in sequence. The SEM images of repeatability experiments are shown in Figure 19 (b,c). Due to the random nature of the bSi fabrication process, the fabricated structures are never 100% identical and possess small variations. The three samples fabricated at different stages were quite similar and it can be seen from SEM images in Figure 19 that the magnitude of structural variations is small.

Figure 19. Repeatability of the process. SEM images of experiment number 1 repeated twice. (Publication 1).

These four types of bSi shown in Figure 18 were used as a baseline for fabricating bSi structures with different morphologies. For publications 2-6, a combination of Type 2 and Type 3 was used to fabricate high aspect ratio micro and nanostructured bSi. For Publication 7, short dense structures were produced by using parameters from Type 2 and Type 4 and slightly higher CCP power.
4.2 Patterned wetting

The morphology of bSi is responsible for different wettability characteristics compared to planar Si substrate. The roughness can enhance hydrophobicity or hydrophilicity depending upon the nature of the bSi surface. Due to the surface topography, bSi after ICP-RIE shows more hydrophilic behaviour than planar Si. On the other hand, when a low surface energy hydrophobic coating is deposited on bSi, the surface becomes superhydrophobic with low CA hysteresis. The details of hydrophilic, hydrophobic and superhydrophobic behaviours are discussed in Chapter 2.

Using bSi, patterned wetting was achieved by fabricating patterns with significant contrast in CA. Superhydrophobic-hydrophobic, superhydrophobic-hydrophilic and superhydrophobic-superhydrophilic patterns were produced by optimising the fabrication techniques. The patterning techniques, droplet confinement, and self-alignment are discussed in the following section.

Photolithographic patterning

The process steps for fabricating a superhydrophobic substrate with hydrophobic/hydrophilic patterns are shown in Figure 20.

![Figure 20](image)

Figure 20. Process steps for fabricating substrate for droplet confinement. a-d) Superhydrophobic bSi substrate and hydrophobic patterns, a-e) superhydrophobic bSi and hydrophilic patterns. (Publications 2 and 4)

First, a photolithographically defined AZ5214E resist mask was used to etch PECVD SiO2 in RIE, shown in Figure 20(a, b). Next, AZ5214 was removed and bSi was formed using ICP-RIE (Figure 20c). After bSi formation, a low surface energy fluoropolymer hydrophobic coating was deposited, which covered both SiO2 protected planar areas and bSi (Figure 20d). In an additional step, the fluoropolymer hydrophobic coating is lifted-off from the patterns by BHF (Figure 20e). This treatment removes SiO2 from the patterns and produces hydrogen terminated clean Si. Upon exposure to the air, the water vapours and oxygen from ambient contribute to native oxide formation. [108] Details of process parameters for each step are explained in Chapter 3.

Figure 21 shows the SEM images of fabricated patterns. The majority of the substrate is a combination of bSi with low surface energy fluoropolymer coating (Figure 21a). In Figure 21b, the patterns are composed of the
fluoropolymer coating on a planar substrate, whereas in Figure 21 c, the patterns are planar Si with native oxide.

![Figure 21. SEM image of fabricated patterns, a) Top view of the fabricated structures of square patterns, b) Magnified and tilted cross-section view of patterns and bSi substrate with fluoropolymer coating, c) patterns with native oxide and the fluoropolymer coated the bSi substrate. (Publications 2 and 4)](image)

The insets in Figure 21 (b, c) show the transition from the pattern to the bSi substrate. The solid edge between the pattern and the substrate composes a well-defined boundary line with a height difference. For hydrophobic patterns, the edge height is a combination of bSi height, Si etched and the PECVD SiO₂ thickness. In the case of hydrophilic patterns, the edge height is a combination of bSi height and Si etched minus the thickness of fluoropolymer coating.

The wettability characteristics of photolithographically patterned substrates are shown in Figure 22. As shown in Figure 22a, fluoropolymer coated planar patterns are hydrophobic (CA = 118 °, CA > 90°). Low surface energy fluoropolymer coating changes the chemical composition of the substrate and reduces wetting. [109] The fluoropolymer coated bSi substrate is superhydrophobic (CA = 179 ± 1°, CA > 150°), shown in Figure 22b. The roughness of bSi combined with hydrophobic fluoropolymer coating leads to a composite state where the droplet sits on roughness features with air trapped underneath. [68] Patterns with native oxide and no fluoropolymer coating are hydrophilic (CA < 90°).
Figure 22. Wettability characteristics of fabricated structures, a) hydrophobic receptor sites with CA of 118 °, b) superhydrophobic bSi with CA above 150 °. (Publication 2)

Direct patterning

The direct patterning of a substrate with extreme wetting contrast was performed using a programmable scanning beam in an ESEM (Publication 5). The process steps are shown in Figure 23. As shown in Figure 23a, tall spiked bSi was formed in ICP-RIE using the same parameters as bSi used in photolithographic patterning. Next, the parylene-C coating was deposited on top of bSi using vacuum deposition system, shown in Figure 23b. The parylene-C coated bSi was fluorinated in RIE, Figure 23c. In the last step shown in Figure 23d, the substrate was subjected to scanning electron beam through water vapours.

Figure 23. Direct patterning in ESEM, a) bSi fabrication, b) parylene-C deposition, c) fluorination of parylene-C in a RIE system using fluorine plasma, d) modification of fluorinated parylene-C using scanning electron beam in the presence of water vapour. (Publication 5)

The surface morphology and profile of the direct patterning process is shown in the SEM, AFM, and optical microscope images in Figure 24. Parylene-C process is known for good conformal nature and the deposited material seamlessly adopts the surface profile of bare bSi (Figure 24a). The fluorination of parylene was performed in SF$_6$ plasma in RIE, where the overall thickness was slightly reduced due to ion bombardment. Figure 24b shows the parylene-C coated bSi after fluorination. The surface morphology after scanning electron beam treatment in water vapour using ESEM was inspected in SEM and optical microscope. No morphological difference was observed in SEM and under the optical microscope the patterns were invisible without water droplets. However, as shown in Figure 24c, under UV illuminated microscope the structures were clearly visible due to optical interference of fluorinated and non-fluorinated film [110]. The AFM data scan in Figure 25d shows that the e-beam treatment with water vapour in ESEM does not induce morphological changes.
The wettability characteristics of the fabricated substrate after direct patterning are shown in Figure 25. The fluorinated parylene-C coated bSi substrate (Figure 25a) is superhydrophobic (CA = 162°). The parylene-C coated bSi without fluorination is hydrophobic (CA = 130°). The superhydrophobicity of the substrate stems from the amplification of intrinsically hydrophobic parylene-C (CA = 90°). The fluorination of parylene-C leads to the formation of new fluorine-containing groups which increase the chemical inertness (by lowering surface energy) and therefore enhancing the hydrophobicity. [111]
The treated substrate (Figure 25b) is superhydrophilic (CA = 10°) and therefore exhibits a huge contrast with the superhydrophobic surroundings. The radical changes to the wetting properties of the surface are attributed to the changes in surface chemistry. The XPS measurement data showed that a uniform fluorine rich organic layer was present before the treatment. After the treatment, nitrogen was detected and a reduced F content compared to Cl was observed. However, the depth distribution of F was same on treated and non-treated areas. This indicated that the modified Cl and N material did not form a continuous film, but rather open chains and clusters. These domains are polar and hydrophilic in nature and with reduced F and pronounced surface roughness lead to the superhydrophilic substrate.

The ESEM exposure parameters can be varied to achieve different geometries and superhydrophilic patterns resolution down to 1 μm. The exposure dose influences the hydrophilicity and a varying degree of wettability can be achieved by changing the dose. Gradually changing the dose during scanning produces surfaces with a gradient in wettability, where highest dose leads to complete wetting.

The direct patterning using ESEM in water vapour is different from O₂ plasma induced modification of parylene-C. In O₂ plasma treated parylene-C, the atomic percentage of oxygen increases and formation of new functional groups leads to increased polarity, surface energy and therefore results in enhanced wettability. Furthermore, the O₂ treated parylene-C is known to restore its hydrophobic nature to a certain extent. The measurements results after direct patterning in ESEM did not show a noticeable difference in oxygen content. Also, the modified superhydrophilic patterns were persistent over a long period of time.

**Droplet confinement**

The droplet confinement inside a certain pattern is due to a pattern boundary line formed by a large wetting contrast (chemical discontinuity) or a topographical edge (geometrical discontinuity). In the case of wetting contrast, the patterns with a smaller CA (θ<sub>γ</sub>) are more wettable than surroundings with higher CA (θ<sub>out</sub>). In such circumstances, the dispensed droplet prefers to sit inside more wettable patterns. The droplet spreads towards the boundary of the pattern and upon contact forms a thin liquid layer which mimics the pattern shape. Under such conditions, the Young’s equation (Equation 1) does not hold and a droplet can assume a range of contact angles (θ<sub>γ</sub> < θ < θ<sub>out</sub>), depending on the liquid volume and the shape of the pattern. Where, θ is the contact angle of confined droplet at the boundary of wettable and non-wettable pattern. The wetting behaviour is shown in Figure 26a.

In the case of a topographical discontinuity shown in Figure 26b, the dispensed droplet (with a CA = θ<sub>γ</sub>) proceeds towards the topographical
Results and applications

Once in contact, the confined advancing droplet can adopt a range of contact angles ($\theta$), which can be described by Gibb's inequality: [116]

$$\theta_Y < \theta < (180 - \theta_P) + \theta_Y$$ (4)

![Figure 26](image.png)

**Figure 26.** Droplet confinement inside a pattern, a) Non-homogeneous surface chemical chemistry. Pattern boundary composed of chemical discontinuity, i.e. the inside of the pattern is more wettable and is surrounded by low wettability surfaces, b) topographical sharp edge composing the pattern boundary, where the chemical composition of the surface is homogeneous. [64] [116]

In equation 4, $\theta_P$ is the angle of topographical boundary. The confinement behaviour is shown in Figure 26b. The upper limit of the CA ($\theta_c$) can be calculated by following equation: [117]

$$\theta_c = (180 - \theta_P) + \theta_Y$$ (5)

Once the droplet reaches $\theta_c$, the confinement is decided by the value of $\theta_P$. If $\theta_P \leq \theta_Y$ so that $\theta_c > 180^\circ$, the $\theta$ will reaches $180^\circ$ with increased volume and will stay confined until gravity becomes appreciable. On the other hand, if $\theta_P > \theta_Y$ so that $\theta_c < 180$, the droplet with reach value of $\theta_c$ with increased volume and then spread down the edge. The Gibb's inequality does not consider the topographical height difference ($h$) shown in Figure 26b. Experimental studies have shown that for $h < 2\mu m$, maximum value of $\theta_c$ of confined droplet decreases with decreasing height. [118] On the other hand, for $h > 2\mu m$, the value of $\theta$ is roughly independent of the height. [114]

The photolithographic patterned wetting scenarios shown in Figure 20 combine both techniques of droplet confinement, i.e. wetting contrast and topographical edge. In the case of hydrophobic patterns (CA = $118^\circ$) and superhydrophobic surroundings (CA = $180^\circ$), the fluoropolymer coating is uniformly deposited and the surface is chemically homogeneous (Figure 22a). The topographical edge composes a height difference excess of 3$\mu m$ with $\theta_P > 100^\circ$. Based on equation 4, $\theta_c > 180^\circ$ and therefore an increased volume will keep the droplets confined until gravity takes over. Figure 27a shows experimental demonstration where a remarkably large droplet is confined on hydrophobic pattern with superhydrophobic surrounding.

In the case of hydrophilic patterns (CA = $52^\circ$) and superhydrophobic surrounding (CA = $174^\circ$) shown in Figure 20 (a-e), the surface of the patterns is a native oxide and the rest of the substrate is fluoropolymer on bSi. The surface is chemically non-homogeneous. The patterns edge height difference is greater than 2$\mu m$ and the sidewall angle is $>100^\circ$. According to Gibb's inequality the $\theta_c$ is lower than $180^\circ$ and therefore at $\theta_c$ further increase in
volume should tumble the droplet along the edge. However, the fluoropolymer coated bSi surface has a huge wetting contrast with the hydrophilic patterns. Therefore with increased volume, the droplet prefers hydrophilic patterns and stays confined for values of $\theta$ higher than $\theta_c$. Figure 27b shows array of large droplets confined to hydrophilic pads on a superhydrophobic substrate over an entire 100mm wafer.

Figure 27. Droplet confinement, a) hydrophobic patterns, superhydrophobic surrounding, (Publication I) b) hydrophilic patterns superhydrophobic background.

In the direct patterning of extreme wetting contrast shown in Figure 24, there is no topographical change at the boundary of the patterns. The chemical nature of the exposed patterns is modified and results in a droplet confinement based on huge wetting contrast. Figure 28 shows the condensation and confinement of water film on superhydrophilic patterns formed by direct patterning.

Figure 28. Condensation of water on superhydrophilic patterns surrounded by the superhydrophobic substrate. Scale bar 100 $\mu$m. (Publication 5)

**Self-alignment**

Droplet confinement to photolithographic patterned substrates (Figure 21) was used to demonstrate the self-alignment of microchips to desired patterns (receptor sites). Hybrid micro-assembly platform was employed to control, deliver and manipulate the microchips and furthermore record the self-alignment process. Typical self-alignment process in a hybrid micro-assembly is shown in Figure 29, consisting of droplet confinement to the receptor sites followed by the microchip delivery and self-alignment.

First, a dispensed droplet is confined to the receptor site, depicted in Figure 29a. Next, as shown in Figure 29b, a microgripper brings a microchip in the vicinity of the receptor site at an initial bias (the difference between releasing
and target position). Microchip released with initial bias forms a liquid meniscus (Figure 29c). Upon release, the stretched liquid meniscus generates a restoring force, which moves the microchip towards the receptor site to minimise the surface energy of meniscus. The surface energy of meniscus minimises according to the shape of the confined droplet (Figure 29d). In the case of a water droplet, the microchip is aligned but not permanently bonded (Figure 29e).

Figure 29. Self-alignment using hybrid micro-assembly setup, a) droplet confinement to the receptor site, b) microchip manipulation by a microgripper, c) microchip released with some overlap to the receptor sites, d-e) microchip self-aligns and bonds to the receptor site. (Publication 2)

In publication II, hybrid micro-assembly setup was employed for the self-alignment on square (200μm × 200μm) hydrophobic receptor sites using microchips with matching dimensions and 50μm thickness. The results are shown in Figure 30. The microchips were fabricated using SU-8 epoxy-based negative photoresist material. Both adhesive and water droplets were used for the self-alignment. Figure 30 (a-c, i-k) show the top view and Figure 30 (d-f, l-n) show the cross-section view of the alignment process. Figure 30 (g, h) and Figure 30 (o, p) show the edge detection for the measurement of alignment accuracy. High alignment accuracy (around 2μm) was achieved at large bias, i.e. 49% and 60% microchip overlap with receptor site for water and adhesive droplets, respectively.

Figure 30. Self-alignment results, a-h) Self-alignment using water droplet, a-c) Top view of the alignment process, d-f) side view of the alignment process, g-h) measurement of alignment accuracy with large initial bias. i-p) Top and cross-sectional images of self-alignment using adhesive droplet. (Publication 2)

The complete wetting of the receptor sites is necessary to achieve a successful self-alignment. The hydrophobic nature of receptor sites can contribute to incomplete wetting throughout the self-alignment process. Such
a scenario leads to microchip misalignment. Figure 31 (a1-a4) shows the top view, whereas Figure 31 (b1-b4) shows the cross-section view of such microchip misalignment. Upon release (Figure 31(a3/b3), microchip moves towards the incompletely wet receptor site and stops before complete alignment. Also, the reduced wetting of the hydrophobic receptor sites leads to a lower restoring force of the meniscus, which is not sufficient for aligning the microchip to the hydrophobic receptor sites.

Figure 31. Self-alignment failure. a1-a4) Top view of misalignment, b1-b4) Side view of misalignment. The receptor site contains a large un-wetted area. The restoring force of hydrophobic receptor site is not enough to align the microchip. (Publication 3)

In publication 3, two different techniques were used to solve the problem of poor wetting of hydrophobic receptor sites. In the first technique, demonstrated in Figure 32 (a1-a4/b1-b4), an excess amount of water was used to achieve a complete droplet confinement to the hydrophobic receptor sites. Reliable self-alignment can be achieved with this technique. The self-alignment duration is longer due to a significant increase in water droplet evaporation time.

Figure 32. Self-alignment techniques for hydrophobic receptor sites, Top view (a1-a4) and side view (b1-b4) of self-alignment using excess water droplet volume (8nl). Side view (c1-c4) and top view (c1-c4) of self-alignment using normal droplet volume (0.9nl) and external pressure. (Publication 3)

In the second technique demonstrated in Figure 32 (c1-c4/d1-d4), utilises a normal droplet volume. Initially, the dispensed droplet did not wet the receptor site completely (Figure 32 (c1)). Once in contact with water droplet and before the release, the microchip was pressed with microgripper to spread the droplet onto the receptor site (Figure 32 (c3/d3)). The pressing improved the wetting of hydrophobic receptor site and upon release, the surface tension aligned the microchip to the receptor sites. The self-alignment duration was lower compared to earlier technique with an excess amount of water droplet volume. Both post-fabrication techniques to achieve the improved wetting of receptor sites demonstrated in publication 3 played an important role for successful alignment.
In publication 4, the wetting of receptor sites was improved and self-alignment of microchips to hydrophilic receptor sites with superhydrophobic surrounding substrate was demonstrated. Photolithographic patterning process is shown in Figure 20(a-e). Hydrophilic receptor sites were composed of oxidised Si whereas fluoropolymer coated bSi was used as a superhydrophobic surrounding substrate. The hybrid micro-assembly technique was modified and indirect water droplet and microchip delivery mechanism were used to demonstrate the self-alignment. The procedure of self-alignment is shown in Figure 33(a1-a6). The self-alignment results using SU-8 microchips with matching receptor sites are shown in Figure 33(b1-b6).

As shown in Figure 33 (b2), when the droplets fall on the substrate, droplet confinement to hydrophilic receptor sites leads to a uniform film of water on top of hydrophilic receptor sites, whereas, the superhydrophobic surroundings permits discrete droplet formation only. Under continuous droplet deposition, the droplets between the microchip and the growing water film on hydrophilic receptor sites form a meniscus, shown in Figure 33 (b3). The meniscus dragged the microchip towards completely wet receptor site in order to lower its surface energy, shown in Figure 33 (b4-b5). The meniscus reaches...
equilibrium position when the microchip is stopped after complete alignment to the receptor site, shown in Figure 33 (b6).

This technique takes advantage of the superhydrophobic characteristics of fluoropolymer coated bSi (surrounding substrate). The water droplets do not spread on the background substrate and greatly enhance the capillary driven self-alignment process. The low adhesion and friction characteristic of the superhydrophobic substrate were easily overcome by capillary forces to self-transport the microchips towards the receptor sites. The self-alignment duration in this technique is significantly higher than other techniques with a direct microchip and droplet delivery to the receptor sites.

4.3 Optical enhancement

The nanostructured bSi surface exhibits exceptional anti-reflection properties in the visible spectrum and also a strong light trapping in the NIR, described in Figure 6 of chapter 2. The reduced reflectance by bSi is due to a variety of phenomena, which are dependent on the size and shape of bSi features. The details of the observed behaviour are discussed in chapter 2. In Publication I, the optical properties (reflectance) of two different types of bSi was measured in the wavelength range of 220 nm - 500 nm. The reflectance spectrum along with the SEM images is shown in Figure 34.

![Figure 34](image)

Figure 34. Reflectance spectra of a) bSi with very high aspect ratio tall structures, b) brown Si with the same shape but reduced height which makes them brownish with the naked eye. (Publication 1)

As shown in Figure 34, the reflectance of two different types of bSi varies significantly in the wavelength region of 200 nm – 500 nm. For the recorded
spectra, the wavelength of incoming light was comparable to the correlation length of bSi features. The reflectance spectrum of tall dense spikes shown in Figure 34a shows remarkably low reflectance compared to bSi shown in Figure 34b. The bSi shown in Figure 34a has higher correlation length and surface structures composed of deep and steep sidewalls, which reduces the backscattering and enhances the coupling of light to different propagating angle. In the case of bSi shown in Figure 34b, the structures are smaller and therefore exhibit higher backscattering and reflect more light. The bSi appears brown with the naked eye and is therefore termed as brown Si (brSi) in publication 1.

The anti-reflection behaviour of bSi changes when the wavelength of incoming light reaches NIR (more dramatically around 1000nm). The wavelength region corresponds to photon energies lower than Si bandgap and therefore the light does not interact similarly as lower wavelengths.

To extend the anti-reflection of bSi beyond UV-VIS, CVD of PyC was combined with bSi in publication 6 (shown in Figure 36b). The tall micro and nanostructured bSi combined with highly absorbing carbon film enabled a material with wide band anti-reflection. Compared to the bSi and brSi demonstrated in Publication 1, the bSi used in this work had tall bSi features with several levels of structural hierarchy. The tall features were chosen to enhance the interaction between broadband of incoming wavelengths and bSi.

The bSi substrate before and after the PyC coating is shown in Figure 35. The tall bSi features possess multiple levels of structural hierarchy (Figure 35a). The magnified view (Figure 35b) shows the fine details of nanostructures on tall bSi features. After PyC deposition (Figure 35c), the structure of bSi remains unchanged as CVD PyC does not compromise the structural integrity of the surface. The magnified view in Figure 35d shows the exceptional film growth in extremely narrow details of bSi nanostructures and negligible roughness introduced by the CVD of PyC on bSi.

The reflectance spectra of Si and bSi with and without PyC coating is shown in Figure 36. As can be seen from Figure 36a, the reflectance of Si increases significantly in NIR and saturates to higher values in the range of 1200 nm-2000 nm. This is attributed to low absorption in that wavelength range and
the majority of incoming light is either reflected or transmitted. The bSi shows a similar trend but with different magnitude of reflectance, shown in Figure 36b. It can be seen that the reflectance of bSi is remarkably lower to Si in UV-VIS, however in NIR and above, bSi shows similar behaviour as bare Si.

The total reflectance of PyC on bare Si is shown in Figure 36a, where the reflectance of the ultrathin layer (25 nm) is almost independent of wavelength (400 nm - 2000 nm). The deposition of PyC coating on bSi leads to a substrate with remarkably low reflectance throughout the incident wavelength range. As shown in Figure 36b, the reflectance is flattened to very small values. Compared to bSi, the PyC coating on bSi also suppresses the reflectance in UV-VIS (300 nm - 800 nm), shown in Figure 36c. The effect on reflectance, however, is remarkable at NIR and above. As shown in Figure 36d, the PyC coated bSi shows reflectance below 0.5%, which is incredibly low compared to bSi, Si, and PyC on plain Si.

![Figure 36. Reflectance spectra of, a) bSi and PyC coated bSi b) bSi and PyC in UV-VIS, c) bSi and PyC coated bSi NIR and above d) Si and PyC.](Publication 6)

The remarkably low reflectance is attributed to the amplification of optical behaviour of the planar PyC film. Unlike Si, the planar PyC films (20 nm-30 nm) have lower transmission in the wavelength range of 1000 nm - 2000 nm and the incoming wavelengths are not only reflected but also absorbed [85]. Combined with the surface topography of bSi (Figure 35a), the PyC coated bSi suppresses the reflectance in the wavelength range of 1000 nm – 2000 nm, shown in Figure 36d. As shown in Figure 35d, the surface topography of bSi is not compromised by PyC deposition process. The PyC coated bSi enhances the interaction of incoming light with the substrate, especially in the wavelength range of 1000 nm-2000 nm. The pronounced interaction leads to reduced transmission and the incoming light is coupled to different propagating angles. The backscattering is low and the propagating and coupled light is ultimately absorbed. The effect is depicted as the extremely low reflectance in the entire wavelength region.
The remarkable optical behaviour of bSi and a possibility to fine tune the surface topography was investigated for SERS in publication 7. In order to evaluate the influence of bSi surface structures, ICP-RIE parameters were varied to fabricate two types of bSi. Thin Ag films with varying thicknesses were chosen as SERS-active metal. Figure 37 shows the SEM images of bSi with Ag on top. The BS01 substrate shown in Figure 37a contains smaller features with average base width and height of 180 nm and 450 nm respectively. The BS02 substrate shown in Figure 37b contains large pyramid like spikes with average base width and height of 1.02 μm and 1.45 μm, respectively.

In order to evaluate the SERS enhancement ability, rhodamine 6G (R6G) probe molecule layer was deposited on BS01 and BS02. Figure 38 shows the Raman spectra of BS01 and BS02. It can be observed that both substrates demonstrate isolated Raman peaks for R6G. However, under the same incident beam, the Raman signal from BS01 is stronger than BS01. The small and dense features of BS01 offer larger excitation area compared to larger BS02 features which correspond to a higher number of localised hot spots and therefore larger SERS enhancement. Also, the sidewall angle of BS01 is higher and allows improved deposition of SERS active material during e-beam evaporation. Small, dense spikes with large sidewall angle in BS01 altogether allow higher SERS sensitivity.

In order to evaluate the effect of Ag thickness for SERS activity of BS01, five different thicknesses of Ag were evaporated on BS01. Figure 39 (a-f) shows the
morphology of BS01 with different thicknesses. Based on surface morphologies shown in Figure 39 (a-f), the thicknesses can be divided into three categories, i.e. thin films of 35 nm - 55 nm (Figure 39 (b, c)), intermediate films of 80 nm - 100 nm (Figure 39 (d, e)), thick film of 150 nm (Figure 39f). With thin layers, the sidewalls of BS01 have randomly distributed nanoparticles. The intermediate thickness (80 nm - 100 nm) contains a thin film and nanoparticles on the sidewalls of BS01. For the thicker film, the film is formed on the sidewalls and the roughness of BS01 is flattened. All the layers on bSi contain a distinctive bead at the top of the peaks, where the size of the bead increases with increasing thickness.

The Raman measurement results with different Ag thickness are shown in Figure 39g. Without Ag coating on plain Si, there is no enhancement. With thin coatings of 35nm-55nm, the recorded spectra show SERS enhancement. The enhancement is due to the coupling of incident light into localised surface plasmons between Ag nanoparticles. The particles are randomly distributed and the penetration of light into bSi leads to lower intensity of surface plasmons and therefore lower SERS enhancement. With an intermediate

Figure 39. BS01 with different Ag thicknesses, a-f) SEM images of BS01, 35nm Ag, 55 nm Ag, 80 nm Ag, 100 nm Ag and 150 nm Ag. Scale bar is 200 nm. g) Raman spectra of R6G with different Ag coating on BS01 in comparison with plain Si. The peak numbers correspond to typical Raman peaks of R6G probe molecule. (Publication VII)
depth of 80 nm - 100 nm, the thin Ag film underneath the nanoparticles reduces penetration of light into bSi. The intensity of surface plasmons is higher and contributes to the strongest SERS signal. An increase in Ag thickness to 150 nm leads to a smoother surface profile, eliminating the nanostructures on the sidewalls. The surface plasmons are significantly reduced and appear as a low Raman signal in Figure 39f. Based on these observations, best SERS results can be achieved by optimised thickness and improved nanostructured sidewall profile. The result is also shown as 80 nm Ag film on BS01 in Figure 39f.

The use of R6G for measuring the SERS enhancement ability is discouraged in Raman community. Complexities due to the employment of R6G as a sensing molecule are highlighted in Chapter 2. At the time of Publication VII, inconsistencies arising from R6G were not considered and therefore the published data contains enhancement capability of SERS template with R6G as a sensing molecule. The results presented in Publication VII are not valid for establishing a true enhancement capability of SERS template. The presented data also lacks a flat Ag reference sample. However, the results from Publication VII are applicable for establishing a relative enhancement. The result also highlights the influence of difference thickness of Ag.
5. Summary and outlook

The research work presented in this thesis describes process development for bSi and enhancement of its intrinsic properties for several application areas. In this work, the bSi formation was performed using cryogenic ICP-RIE only. In the beginning, DOE was used to study the influence of process parameters on the bSi formation. The study highlighted the influential rank of process parameters on bSi formation. The results were used to establish guidelines for fabricating different types of bSi, each type having a different shape, size and density of the bSi structures.

The hierarchical structural topography of bSi was used to modify the wetting behaviour of the surface. Compatibility of the bSi process with standard semiconductor processing allowed side by side fabrication of patterns with extreme wetting contrast. Upon dispensing, the water droplets preferred more wettable areas and produced patterned wetting. This was achieved by two different pattern definition techniques. In the first technique, standard microfabrication steps were adopted to fabricate substrate template with hydrophobic/hydrophilic patterns and superhydrophobic surroundings. Surface tension driven self-alignment of microchip was recorded on the fabricated template using hybrid micro-assembly platform. Different microchip delivery mechanisms were examined and the self-alignment results were reliable and repeatable. In the second technique, direct pattern definition to fluorinated- parylene-C coated bSi was performed in an ESEM using e-beam and water vapour. E-beam treated areas were superhydrophilic whereas untreated areas remained superhydrophobic. Due to the large wetting contrast, the water droplets stayed confined to e-beam exposed superhydrophilic patterns. This technique is useful for fabricating patterns with extreme wetting contrast at extremely high resolution.

The variation of structural topography between different types of bSi induced different optical response. The size, shape and density of bSi structures strongly influence the interaction of light. In UV-VIS, extremely low reflectance was recorded from bSi with optimised surface structures. However, the working window of Si is limited and similarly bSi also becomes transparent to incoming radiations at NIR and above. In order to improve the antireflection behaviour of bSi (from UV-VIS and above), the bSi substrate was coated with PyC coating. The conformal coating did not compromise the surface topography of bSi micro and nanostructures. The reflectance of bSi was flattened and suppressed throughout the measured spectrum (400 nm – 2000 nm). For plasmonic enhancement, a thin film of Ag was deposited on a
bSi type with relatively smaller surface features. Different Ag thicknesses were examined and improved SERS sensitivity was recorded using a combination of optimised bSi surface structure and Ag thickness.

The findings of presented in this thesis highlight the diversity of applications that can be achieved with bSi. This work shows a glimpse of scientific interest bSi has seen in the last decade. Relatively low cost and quick fabrication process make bSi an ideal platform for transferring applications towards industrial scale. As a material, bSi holds great potential for the future and is already beginning to find its way inside commercial devices. [119]

On the other hand, the surface topography of bSi brings a serious challenge. The micro and nanostructured surface features are mechanically vulnerable and can break even with a gentle mechanical contact. A lot more attention is needed to overcome this limitation. Mechanical durability of bSi is vital to sustain the properties bSi is known for.
References


References


