Control and characterization of wetting at micro- and nanoscales

Ville Liimatainen
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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 TU2 of the school on the 6th of February 2017 at 12 noon.

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Abstract

Wetting of surfaces is a fundamental research topic related to phenomena that are ubiquitous, from everyday life to science and technology. Liquid-repellent surfaces with low wettability can be found in textiles, kitchenware, eyeglasses and other optics, car windcreens and mirrors, outer surfaces of buildings and structures, and in various plants and insects in nature, which often provide inspiration for artificial repellent and super-repellent surfaces. Synthesizing and characterizing such surfaces is of great interest for both scientific studies and practical applications.

Despite remarkable advances in the past few decades, challenges in wettability characterization and controlled wettability still remain. Measuring the wettability of superhydrophobic surfaces in a reliable and repeatable manner is difficult using traditional optical contact angle methods. In wetting control, one challenge is limiting the wetting of low surface tension liquids, such as oils and solvents, which easily spread on most surfaces. Another challenge is patterned wettability, where well-defined areas should have extreme differences in wetting properties.

This thesis presents results in characterization of superhydrophobic surfaces, and wetting control through patterning and its applications in hybrid microassembly. Firstly, a force measurement-based method for characterization of superhydrophobic surface wettability is described. Interaction forces between a droplet and the surface are measured using high resolution to extract wetting and adhesion properties. The method can be applied in a scanning manner to map and reveal small local variations in wettability.

A method for confining low surface tension liquids based on surface topography was also developed. The technique is realized using well-established silicon microfabrication techniques, and is applicable from the macroscale to the microscale. As the method is based purely on surface topography, it is widely applicable to different surface materials.

Finally, a scanning electron beam method for accurate (sub-μm), high wetting contrast water wettability patterning is introduced. The results also reveal the possible wettability-modifying effects of electron beams in environmental scanning electron microscopes (ESEM), which are well-established tools used in various micro- and nanoscale wetting studies.

Keywords wettability characterization, wetting patterns, droplet self-alignment

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Ville Lähtäinen

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Viime vuosikymmenten edistyksestä huolimatta kostumisominaisuuksien mitaamisessa ja hallinnassa on edelleen haasteita. Superhydrofobisten pintojen kostuvuuden luotettava ja toistettava mitaaminen on hankalaa perinteisellä optisella kontaktikulumitaauksella. Kostumisen hallinnassa eräs haaste on matalan pintatäytyvyyden nesteiden kostumisen rajoittaminen. Tällaisia nesteitä ovat esimerkiksi öljyt ja monet luottimet, jotka levittyvät helposti useimmilla pinnoilla. Toinen haaste on kuvoitu kostuvuus, jossa tarkkaan määritellään alueilla kostumisominaisuuksid poikkeavat huomattavasti muusta pinnasta.

Tässä väitöskirjatyössä tutkittiin superhydrofobisten pintojen kostumisominaisuuksien mittausta sekä kostuvuuden kuviointia erityisesti mikrokookenpanon sovelluksissa. Aluksi kuvailaan superhydrofobisten pintojen kostuvuuden mitaamiseen meneteltä, joka perustuu vesipisaran ja pinnan välisten voimien mitaamiseen korkealla tarkkuudella. Menetelmällä voidaan kartoittaa pieniä, paikallisissa poikkeamia kostuvuudessa.

Työssä kehitettiin myös pyynnön topografiassa perustuvia menetelmiä rajoittamaan matalan pintatäytyvyyden nesteiden levämistä pinnoilla. Vakiointineilla mikrovalmistustekniikoilla toteutettua menetelmää voidaan soveltaa makromittakaavasta mikromailmaan asti, ja se sopii useille pintaamateriaaleille.

Lisäksi väitöskirjatyössä esiteltään uusi, kohdistettuun elektronisiihkuun perustuva menetelmä kostuvuuden tarkkaan kuviointiin. Tulokset myös osoittavat, että kostumisilmöitä pyyhkäiselyelektronimikroskoopilla tutkittaessa elektronisiihlulla voi olla näytteen kostumisominaisuuksia muokkaavia vaikutuksia.

Avainsanat
kostuvuuden mittaus, kostumiskuviot, pisaran itselähdistus

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I started in the Micro- and Nanorobotics group as a research assistant in the summer of 2007. The first project I was working on was about developing a swallowable capsule for the diagnosis of irritable bowel syndrome (IBS). The way since then has been long and winding, but I have never stopped being fascinated by the various topics and projects explored by the group.

I am most grateful to Prof. Quan Zhou for the opportunity to work in such a talented and interdisciplinary team, and for his guidance and support during the research leading to this thesis. I am also grateful to all past and present members of the Micro- and Nanorobotics group, especially Veikko Sariola. We shared an office for many years, and besides his invaluable help and advice, we had endless discussions about work, hobbies and other interests too. My warm thanks also to Petri Hänninen, Bo Chang, Mirva Jääskeläinen, Antti Virta, Iriris Routa, Janne Venäläinen, Mikko Koverola, Zoran Cenev, Kourosh Latifi, Harri Wijaya and Saeed Karimi for making working in the group always such a pleasure. I am also indebted to collaborators I have had the honor of working with, particularly Maja Vuckovac, Ville Jokinen, Ali Shah, Leena-Sisko Johansson and Prof. Robin Ras.

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Making it this far would never have been possible without the loving support of my family throughout my life. I express my deepest gratitude and love to my parents Anneli and Vilho, and to my sisters Karoliina and Elisa, for always being
there. Finally, I thank my girlfriend Outi, for her love, and the shared adventures past and yet to come.

Espoo, January 2017

Ville Liimatainen
List of Publications

This doctoral dissertation consists of a summary and of the following publications.


Author’s Contribution

All the work was carried out under the supervision of Prof. Quan Zhou, who contributed to design of many of the concepts, experiments and revision of the results and manuscripts.

Publication 1: “Controlling liquid spreading using microfabricated undercut edges”

The author designed the concept and performed the experiments together with Dr. Veikko Sariola, fabricated the structures and wrote the manuscript. Dr. Veikko Sariola contributed to the revision of the manuscript.

Publication 2: “Maskless, high-precision, persistent, and extreme wetting-contrast patterning in an environmental scanning electron microscope”

The author discovered the phenomena, designed and carried out the experiments and wrote the manuscript. Sample surfaces were fabricated by M.Sc. Ali Shah. X-ray photoelectron spectroscopy was carried out by Leena-Sisko Johansson. Atomic force microscopy was done by Nikolay Houbenov. All authors contributed to the revision of the manuscript.

Publication 3: “Mapping microscale wetting variations on biological and synthetic water-repellent surfaces”

The author contributed equally with M.Sc. Maja Vuckovac. They designed and carried out the experiments, analysed the data and wrote the manuscript. The author developed experimental procedures and data analysis methods, and contributed to sample preparation. Dr. Ville Jokinen and M.Sc. Maja Vuckovac designed and prepared most of the sample surfaces. Dr. Ville Jokinen fabricated the probe tip. Dr. Veikko Sariola simulated the concept. Prof. Robin Ras contributed to design of the concept, experiments and revision of the results and manuscript together with Prof. Quan Zhou.

Publication 4: “Microsystem integration using hybrid microassembly”

The author contributed to hybrid microassembly experiments together with M.Sc. Iiris Routa in three industrial case studies: 1) integration of microchips on lead frame; 2) integration of vertical cavity surface emitting laser chips on optical benches; 3) 3D integration of thin dies into 3-layer stacks connected with through-silicon-vias.
Publication 5: “Undercut edges for robust capillary self-alignment in hybrid microassembly”

The author designed and fabricated the structures, carried out experiments and wrote the manuscript. Dr. Veikko Sariola contributed to design of experiments.

Publication 6: “Capillary self-alignment assisted hybrid robotic handling for ultra-thin die stacking”

The author contributed to the design of experiments and data analysis, and wrote the manuscript. M.Sc. Mohamed Kharboutly and M.Sc. David Rostoucher fabricated the samples, carried out the experiments and analysed the data. Prof. Michaël Gauthier revised the manuscript.

Publication 7: “High-accuracy positioning of microchips on patterns with jagged edges using hybrid microassembly”

The author contributed to the design and fabrication of samples.
# Symbols

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<th>Symbol</th>
<th>Unit</th>
<th>Definition</th>
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<tr>
<td>$F_C$</td>
<td>N</td>
<td>Capillary force</td>
</tr>
<tr>
<td>$F_L$</td>
<td>N</td>
<td>Force due to Laplace pressure</td>
</tr>
<tr>
<td>$F_T$</td>
<td>N</td>
<td>Force due to surface tension</td>
</tr>
<tr>
<td>$r$</td>
<td></td>
<td>Surface roughness, ratio of the actual surface area to the geometric surface area, $r \geq 1$</td>
</tr>
<tr>
<td>$R_{1,2}$</td>
<td>m</td>
<td>Principal radii of curvature</td>
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<tr>
<td>$W$</td>
<td>J</td>
<td>Mechanical work</td>
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## Greek symbols

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<tr>
<th>Symbol</th>
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<tr>
<td>$\gamma$</td>
<td>J/m$^2$</td>
<td>Surface energy. For liquids equal to surface tension.</td>
</tr>
<tr>
<td>$\gamma_{SL}, \gamma_{LG}, \gamma_{SG}$</td>
<td>J/m$^2$</td>
<td>Surface energies of the solid-liquid, liquid-gas and solid-gas interfaces, respectively</td>
</tr>
<tr>
<td>$\theta, \theta^*$</td>
<td>°</td>
<td>Apparent contact angle</td>
</tr>
<tr>
<td>$\theta_A$</td>
<td>°</td>
<td>Advancing contact angle</td>
</tr>
<tr>
<td>$\theta_C, \theta_0$</td>
<td>°</td>
<td>Contact angle, Young’s contact angle</td>
</tr>
<tr>
<td>$\theta_E$</td>
<td>°</td>
<td>Equilibrium/static contact angle</td>
</tr>
<tr>
<td>$\theta_R$</td>
<td>°</td>
<td>Receding contact angle</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>m</td>
<td>Standard deviation of alignment error</td>
</tr>
<tr>
<td>$\varphi$</td>
<td>°</td>
<td>Sharp edge angle through the solid</td>
</tr>
</tbody>
</table>
Abbreviations

AFM  Atomic force microscopy
EBL  Electron beam lithography
ESEM Environmental scanning electron microscopy
IC   Integrated circuit
NSOM Near-field scanning optical microscopy
RFID Radio frequency identification
RIE  Reactive ion etching
SEM  Scanning electron microscopy
SU-8 A negative, high aspect-ration photoresist
THCPSi Thermally hydrocarbonized porous silicon
TSV  Through-silicon-via
VCSEL Vertical cavity surface emitting laser
XPS  X-ray photoelectron spectroscopy
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1. Introduction

Wetting is the contact of a liquid with a solid surface, and changes therein. Wetting phenomena are ubiquitous from everyday life to science and technology. Repellent surfaces that impair or prevent wetting altogether can be found in textiles, eyeglasses and other optics, car windscreens and mirrors, kitchenware, outer surfaces of buildings and structures, as well as in various plants and insects in nature, which often provide inspiration for artificial repellent and super-repellent surfaces. The ability to synthesize surfaces with special wettability and to modify existing surfaces has become essential in a wide range of applications in science and technology, such as water collection from humid air [1], droplet arrays for biological [2] and chemical screening [3], lab-on-a-chip [4], fluidic optics [5], surface microfluidics [6], and droplet self-transportation [7].

Wettability of surfaces and mechanisms of wetting have been intensively studied for almost a hundred years now, starting from the groundbreaking work of Wenzel [8] and Cassie and Baxter [9] related to water repellency of materials. For quite some time now, one of the heated topics in the research field of wetting has been super-repellent surfaces that cannot be wetted by liquids. In the case of water, such a surface is said to be superhydrophobic. Superhydrophobic surfaces have many interesting properties, such as self-cleaning [10], antibacterial [11], anti-fouling [12], high or low adhesion [13], anti-fogging [14], anti-icing [15] and anti-corrosion [16].

One challenge related to superhydrophobic surfaces is the characterization of their wettability with high precision. Surface wettability is typically characterized by measuring contact angles when liquid is deposited on the surface. On superhydrophobic surfaces, the water contact angles can be so high that it becomes difficult to reliably distinguish differences between surfaces by traditional optical contact angle measurements. Homogeneity of a superhydrophobic surface is equally challenging to verify as local variations cannot be easily detected. It is the prevailing practice to report only one global value for the advancing contact angle and one global value for the receding contact angle, for one surface. Another common measure of wettability is the sliding angle i.e. the required tilting angle such that a water droplet slides or rolls off the surface. The sliding angle can be very low for superhydrophobic surfaces, less than $1^\circ$ [17], making it hard to measure on specific locations on the surface. Wettability can also be characterized by measuring the normal and in-plane contact forces of droplets on the surface [18], [19]. However, these
forces can be very small and thus difficult to measure on superhydrophobic surfaces.

As wetting and related phenomena have been extensively studied for decades already, the focus is increasingly shifting towards manipulating surfaces to control the wetting properties [20], [21]. Modifying and tuning wettability is a key challenge in many applications, including those listed above. Surface wetting properties can be altered by modifying the surface topography, chemistry, or both. Common, mature techniques include photolithography, reactive ion etching (RIE) [22], wet chemical etching [23], various deposition and coating processes, plasma treatments [24] and modification by energetic beams [25]. Despite the great advances in the past few decades, challenges still remain in achieving controlled wettability. One difficulty is controlling low surface tension liquids, such as oils and solvents, which easily wet most surfaces. Limiting their wetting is therefore more demanding compared to e.g. water that has high surface tension.

Wettability can be modified globally over the whole surface, but often it is required to have well-defined areas with different wetting properties i.e. patterned wettability. Accurate and flexible wettability patterning remains a challenge in many cases. It is usually preferable to have wetting patterns with large contrast i.e. difference in wettability between the patterns and the background. Many wetting applications in micro-, nano- and biotechnology require patterning at small scales, from millimeters down to micro- and even nanometers, due to the small size of objects and/or small surface areas relevant to the application. High-precision patterning methods are therefore needed, but at the same time they should be flexible in terms of pattern shapes, and applicable to a wide range of surfaces and liquids.

1.1 Research objectives

The objectives of the work are to tackle challenges in 1) superhydrophobic surface characterization; 2) wetting control of low surface tension liquids; and 3) accurate, large wetting contrast patterning. Specifically, the following research questions are addressed:

- Can normal force measurements be used to characterize superhydrophobic surface wettability, so that spatial heterogeneity within one surface and small differences between two surfaces with similar wettability could be detected?
- How can the spreading of low surface tension liquids be controlled?
- How to achieve high wetting contrast and high precision simultaneously in water wettability patterning?

1.2 Contributions to the research field

This thesis brings new knowledge of superhydrophobic surfaces, and new methods for wettability characterization and wetting control:
1. A novel method based on force measurements for mapping the wettability of superhydrophobic surfaces. Interaction forces between a droplet and the surface are measured to extract wetting and surface adhesion properties with high resolution. A scanning method is developed that allows mapping of wettability on superhydrophobic surfaces, revealing local variations. New understanding of the fundamental limit of superhydrophobicity is also obtained. While the liquid used in the study is water, the proposed method should work with any combination of liquid and surface that is super-repellent to it.

2. A novel method based on surface topography for confining low surface tension liquids. The technique is applicable from macroscale down to microscale and is realized using well-established silicon microfabrication techniques. As the method is based purely on surface topography, it is widely applicable to different materials.

3. A novel method based on scanning electron beam for accurate (sub-μm) water wettability patterning in an environmental scanning electron microscope (ESEM). The method produces patterns with extreme wetting contrast that persist over a long period of time. It is also maskless, allowing generation of arbitrary patterns. The results also point out possible wettability modifying effects of electron beam in an ESEM, which is nowadays a well-established tool for various micro- and nanoscale wetting studies.

1.3 **Structure of the thesis**

This thesis presents results in characterization of superhydrophobic surfaces, wetting control by two patterning techniques, and applications in hybrid microassembly. Chapter 2 introduces fundamentals of wetting and common wettability characterization techniques, followed by the reporting of a novel method for characterization of superhydrophobic surfaces. Chapter 3 discusses wettability modification and patterning methods, divided in two categories: topographical and chemical. Along with known techniques, two new methods are introduced, one purely topographical and one purely chemical. Chapter 4 presents one prominent application of wetting patterns: surface tension-driven self-alignment. The methods from Chapter 3 are applied to several studies, including real-world industrial applications. Finally, conclusions are drawn in Chapter 5.
Introduction
2. Wettability of surfaces

This chapter introduces fundamental concepts of wetting, and common wettability characterization techniques. A new method for measuring wettability of superhydrophobic surfaces is presented.

2.1 Surface energy and surface tension

Molecules on the surface of a bulk material share less cohesive interactions with the neighboring molecules compared to those inside the bulk (Fig. 1). This leads to excess energy on the surface, which is called surface energy. In the case of a liquid-gas interface, e.g. water-air, attraction between water molecules and air at the surface is smaller than attraction among water molecules inside the liquid. The resulting excess energy at the surface manifests as surface tension, a force along the surface that tries to minimize the area of the interface. In the other cases, e.g. solid-liquid or solid-gas interfaces, the difference in molecular interactions at the interface is referred to as interfacial tension.

Surface energy is defined as energy per unit area, and surface tension as force per unit length. Surface tension plays an important role in all wetting phenomena, especially at small scales where it can be the main force due to scaling of forces. For droplets of liquid smaller than the capillary length...
(e.g. ~2.7mm for water), surface tension starts to dominate and gravity becomes less important or even negligible.

Although surface energy and surface tension are mathematically equivalent, the physical interpretation is different and should not be confused with each other: surface energy is measured on an area, whereas surface tension is measured along a line. Even the early models and equations put forward by Wenzel [8] and Cassie [9] have been later on questioned and lead to great controversy [26]–[30] due to confusion of concepts related to the difference between surface energy and surface tension. Throughout this thesis, the distinction is clarified in each case, even though the same symbol $\gamma$ is used for both, as is the common convention.

2.2 Wetting

Wetting is the study of how a liquid deposited on a solid surface spreads. The area of interest is where the three phases (liquid, solid, gas) contact each other, known as the triple line, or contact line. The angle the liquid outline makes with the solid is called the contact angle, and it is a measure of how well the liquid wets the solid surface. The lower the contact angle, the more easily the liquid spreads on the surface i.e. the more complete is the wetting. Conversely, higher contact angles lead to partial wetting. Contact angle, contact line and the associated interfacial tensions are depicted in Fig. 2.

Figure 2. Definition of contact angle and directions of interfacial tensions.

At equilibrium, the interfacial tensions at the contact line balance out. This can be described by Young’s equation:

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cos \theta_c$$  \hspace{1cm} (1)

where $\gamma_{SG}$ is the solid-gas interfacial tension, $\gamma_{SL}$ the solid-liquid interfacial tension, $\gamma_{LG}$ the liquid-gas surface tension, and $\theta_c$ is the (Young’s) contact angle of the liquid on the surface.

Young’s equation describes the forces at equilibrium, and holds for ideal surfaces i.e. atomically smooth and chemically homogeneous. For such surfaces there is only one contact angle. However, in reality surfaces have roughness that can vary spatially. Moreover, the chemical composition of the surface can also have spatial variations. These differences lead to variation in contact angle when the contact line is moving. Depending on whether the liquid is advancing or
receding on the surface, the terms advancing contact angle (θ_a) and receding contact angle (θ_r) are used, respectively. At equilibrium, i.e. when the contact line is not moving and has settled, the term static contact angle or equilibrium contact angle (θ_e) is used. For any liquid, the advancing contact angle is greater and the receding contact angle smaller than the equilibrium contact angle, respectively. The difference between the advancing and receding contact angles is known as contact angle hysteresis.

Solids with high surface energy, such as glass and silicon, are easily wetted by liquids as it is energetically favorable for the liquid with lower surface energy to cover the high energy surface. On the other hand, solids with low surface energy, e.g. many plastics and fluorinated surfaces, are not easily wetted by liquids. In this case energy minimization leads to smaller contact area (large contact angle) between the relatively high surface energy liquid and the low energy surface. However, the equilibrium contact angle does not depend on surface energy difference at the contact line alone, it is also affected by roughness at the contact line. The relationship between the measured, apparent contact angle of a liquid on a rough surface, and the Young’s contact angle (θ_C), is described by Wenzel’s model:

$$\cos \theta^* = r \cos \theta_C$$

(2)

where \( r \) is the roughness factor i.e. ratio of the actual surface area in contact with the liquid to the apparent, projected wetted area. It follows from Eq. (2) that for rough surfaces (\( r \geq 1 \)), the apparent contact angle \( \theta^* \) is lower than the true contact angle if \( \theta_C < 90^\circ \) and higher if \( \theta_C > 90^\circ \). Roughness of the surface thus enhances wettability for low contact angles and further reduces it for high contact angles. Therefore, large changes in the contact angle can be achieved on rough surfaces by altering the surface chemistry so that the contact angle crosses from one side of the \( \theta_C = 90^\circ \) border case to the other. This effect was demonstrated in PUB2 and will be discussed later in Chapter 3.

In the case of water, if the equilibrium contact angle on a surface is smaller than 90°, then the surface is commonly said to be hydrophilic, while contact angles larger than 90° imply a hydrophobic surface. Further definitions of superhydrophilic for very low contact angles (\( \theta_C < 10^\circ \)) and superhydrophobic for very high contact angles (\( \theta_C > 150^\circ \)), are commonly used. For superhydrophobic surfaces, it is usually further required that the sliding angle is less than 10° [31].

2.3 Work of adhesion

If two phases are separated inside a third phase, e.g. liquid droplet on a solid surface in air (Fig. 3), then two new interfaces are created and one interface is destroyed when the droplet is separated from the surface. The work involved in pulling the volume off the surface is given by:

$$\Delta W = y_{SG} + y_{LG} - y_{SL}$$

(3)

where \( y_{SG}, y_{LG} \) and \( y_{SL} \) are the solid-gas, liquid-gas and solid-liquid interfacial energies, respectively, and \( \Delta W \) is the work of adhesion per unit area. The work
is done by a force in the direction normal to the surface. The force required to break the interface is referred to as pull-off force. Work of adhesion is also involved in the opposite case, i.e. when a volume of liquid is attached to a solid surface, and the corresponding force is called the snap-in force. Substituting Eq. (1) into Eq. (3) yields the Young-Dupré equation:

\[ \Delta W = \gamma_{LG} (1 + \cos \theta_c) \]  

(4)

Work of adhesion can thus be estimated from the surface energy and the contact angle. To determine the work of adhesion for a water droplet on a surface, the shape of the meniscus both before and after separation are required to calculate the relevant surface areas, which can be difficult to do analytically. However, the shape of the meniscus may be computed numerically by e.g. finding the shape that minimizes surface energy of the meniscus using Surface Evolver [32]. Linking the snap-in and pull-off forces to the work of adhesion, and to the contact angle, is discussed next.

![Figure 3. Work of adhesion. Separating a volume of liquid from a solid surface destroys one surface (left) and creates two new surfaces (right), and the difference in the energies before and after separation is defined as the work of adhesion.](image)

### 2.4 Characterization of wettability

The prevalent technique for characterizing wettability of a surface is optical contact angle measurement. In the static sessile drop method, the equilibrium contact angle of a liquid droplet on a surface is directly observed by a camera. The dynamic sessile drop method measures both advancing and receding contact angles by injecting or removing liquid from the droplet through a capillary, respectively. In another dynamic method, the droplet is placed on a surface that is gradually tilted. The advancing and receding contact angles are obtained by observing the front and the rear of the droplet right before it starts moving. The accuracy of these methods can be increased by fitting curves to the droplet outline with the help of image processing techniques. An overview of the different fitting procedures is given by Stalder et al. [33]. Other optical methods include optical reflectometry and contrast interferometry.

While the optical methods can give very accurate results, e.g. ± 0.1° [34], they become challenging for rough, superhydrophobic surfaces. Srinivasan et al. analyzed the accuracy of optical measurements for sessile drops on liquid-repellent surfaces [35] and concluded that as the contact angle approaches 180°, an uncertainty of as small as 1µm in the location of the droplet baseline or
Wettability of surfaces

droplet height can result in an uncertainty in the contact angle as large as 10°. Even though the optical measurements are more accurate for the lower range of superhydrophobic surfaces, i.e. $150° < \theta_c < 170°$, they only work if the surface baseline can be reliably detected. In practice, many interesting natural superhydrophobic surfaces, such as plant leaves or insect wings [36], [37], have curved surface topography and cannot be made flat without destroying them. In these cases the optical methods are difficult or impossible to apply because the surface baseline is not a line or a regular curve, or not visible at all. A difficult case is illustrated in Fig. 4, which shows optical microscope image of a water droplet near the superhydrophobic wing of a butterfly.

Figure 4. The effect of surface topography on optical contact angle measurement. A 1.5μl water droplet near the irregular surface of a butterfly wing, where detecting the surface baseline for contact angle measurement may be difficult.

Another approach to contact angle measurement is the force based Wilhelmy plate method, where a vertically mounted solid plate with identical surfaces on both sides is slowly immersed in and retracted from a liquid of know surface tension. The force during immersion and retraction is measured, yielding the advancing and receding contact angles, respectively, as the surface tension of the liquid and the width of the plate are known. For the Wilhelmy plate method, Extrand estimated that an absolute error of 1μN in the measured force can lead to uncertainties in excess of 10° for contact angles higher than 175° [38]. Furthermore, any topographical or chemical heterogeneities on either side of the plate may cause additional errors. Fabrication of identical, homogeneous surfaces required by the method is very challenging, and impossible for natural surfaces. The method is also not suitable for measuring on different spots on a surface.

In addition to the problems with uneven surfaces, both contact angle measurements and the Wilhelmy plate method lack spatial resolution. It is common to give just one pair of advancing and receding contact angle values for the whole sample, even though on real-world surfaces wettability varies spatially. So far this heterogeneity in the wetting properties of superhydrophobic surfaces has not been systematically investigated.

An alternative approach to characterizing the wettability of superhydrophobic surfaces is to study the forces when a droplet interacts with the surface. Contact
angle hysteresis and friction can be obtained by observing droplet motion on tilted superhydrophobic substrates [39]–[41]. In a recently proposed method, friction of superhydrophobic surfaces was characterized by quantifying the lateral forces when magnetic droplets oscillate on a horizontal surface and dissipate energy [19].

On the other hand, normal forces between a droplet and a surface are related to adhesion. To date, extensive work has been carried out to measure the pull-off force required to separate a liquid droplet from a surface for the purpose of characterizing surface adhesion [42]–[51]. It has been suggested that the pull-off force is a measure of tensile hydrophobicity [52], [53] of the surface. Gao and McCarthy stated that the pull-off force should be a function of only the receding contact angle [53] through the work of adhesion:

$$\Delta W = \gamma_{LG}(1 + \cos \theta_R)$$

where $\gamma_{LG}$ is the liquid-gas interfacial (surface) energy and $\theta_R$ is the receding contact angle. The relation in Eq. (5) has been experimentally verified by Samuel et al. in a study of wetting and adhesion forces between water and various superhydrophobic surfaces [18].

While the pull-off force is a widely applied measure of surface adhesion, snap-in force has received much less attention. Samuel et al. measured snap-in forces for a wide range of surfaces [18]. They showed a relation between the snap-in force and the advancing contact angle. Thus, measuring the normal force during a full cycle of liquid droplet approaching, touching, and then retracting from a surface could potentially be used to extract both advancing and receding contact angles. Such a measurement would be especially useful when characterizing adhesion and wetting properties of superhydrophobic surfaces, where high contact angles and small variations are challenging for the traditional optical measurements. The accuracy of the method would depend only on the accuracy of the force measurement. Normal force measurement is therefore potentially an attractive method for superhydrophobic surface wettability characterization, if the small interaction forces can be detected accurately.

In PUB3, a microforce sensing probe was used in a custom built setup to measure droplet interactions on a surface, with the goal of mapping the spatially varying wetting properties. The concept, scanning droplet adhesion microscopy, is depicted in Fig. 5A-C. The measurement starts with the surface to be probed close to a liquid droplet (e.g. water) pinned on a 1mm diameter, 80μm thick disk made of SU-8 photoresist and attached to the tip of a vertically mounted force sensor. The sample stage starts moving up towards the droplet (Fig. 5B-I), until the droplet touches the surface (snap-in, Fig. 5B-II). After a short time of contact, the stage is then retracted down (Fig. 5B-III) until the droplet separates from the surface (pull-off, Fig. 5B-IV). A typical force curve of one measurement is shown in Fig. 5C. Scanning (i.e. spatially repeating the above process) over an area of interest (Fig. 5D) yields snap-in (Fig. 5E) and pull-off (Fig. 5F) force maps that correspond to local wetting properties of the sample (e.g. a butterfly wing, Fig. 5A), which may depend on the micro- and nanostructure of the surface, and chemical heterogeneity.
Figure 5. Concept of scanning droplet adhesion microscopy. (A) Schematic diagram of the microscope. (B) Snapshots of one measurement on a single micropillar (white arrows indicate direction of sample surface movement), and (C) corresponding typical force curve. (D) Optical micrograph of a scanned area on a butterfly wing with corresponding (E) snap-in and (F) pull-off force maps (black dots denote measurement points with 200μm spacing). The color maps used to visualize the wetting forces are contour plots of the measured force values.

The accuracy and repeatability of the method was calibrated by measuring snap-in and pull-off forces on individual round pillars of 10, 20, 35 and 50μm radii. All pillars were 20μm high and made of silicon, with an undercut silicon dioxide top developed in PUB1 to prevent overflow down the side of the pillar. As the top of the pillar is superhydrophilic (θ_A < 10°), the contact radius is that of the pillar. Volume of the droplet was constant (1.5μL) in all measurements. Ten different pillars were used for each pillar radius, and measurements were repeated ten times on each pillar, amounting to 100 measurements for each pillar size. Larger pillars of 100, 150, 200, 250 and 400μm radii were also measured to further study the snap-in and pull-off forces as a function of pillar radius, with three measurements for each pillar size. The results on the pillars are shown in Fig. 6 together with numerical simulation.
Figure 6. Accuracy and repeatability of normal force measurements on undercut silicon micropillars. (A,B) Snap-in and pull-off forces as function of pillar radius. Number of data points was 100 (10 – 50μm radius pillars) or three (100 – 400μm radius pillars). Solid lines show numerical simulation results, and error bars denote standard deviation in force.

The forces on the 10 – 50μm radii pillars reported in Fig. 6 were calculated as a mean of mean values over the ten different pillars, and the error was calculated as the pooled standard deviation. The values are listed in Table 1, together with analysis of variance (ANOVA). The high F-values indicate that pillar-to-pillar variation is much larger than within-pillar variation, while the extremely low p-values mean very small probability of getting these results by chance.

Table 1. Analysis of variance (ANOVA) of the force calibration on silicon micropillars with different pillar radii. The pooled standard deviation (error) is in the same order of magnitude for all pillar radii, and is comparable to the sensor noise (5nN).

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<th>10μm</th>
<th>20μm</th>
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<th>50μm</th>
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<td><strong>Snap-in force</strong></td>
<td></td>
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<tr>
<td>(mean ± pooled std)</td>
<td>125.9 ± 6.6nN</td>
<td>173.5 ± 4.9nN</td>
<td>296.8 ± 7.4nN</td>
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<td>p-value (ANOVA)</td>
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<td>2.92 × 10⁻⁴⁴</td>
<td>9.32 × 10⁻¹¹</td>
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<tr>
<td><strong>Pull-off force</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(mean ± pooled std)</td>
<td>4.6064μN ± 5.3nN</td>
<td>9.2710μN ± 6.6nN</td>
<td>15.9226μN ± 11.2nN</td>
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<tr>
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<td>2.84 × 10⁻³⁰</td>
<td>1.55 × 10⁻³⁶</td>
<td>3.42 × 10⁻¹⁶</td>
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The noise of the sensor when the droplet is on the tip was measured to be 5nN. Comparing this value to the errors in Table 1 shows that the variation within each pillar can be largely attributed to sensor noise as it accounts for a major part of the error numbers. The measurement method is therefore quite repeatable. Variation in the snap-in and pull-off forces between the pillars are attributed to fabrication defects, possible contamination particles from ambient air, and to randomness in the wetting process itself.

The forces in Fig. 6 grow with the pillar (contact) radius. This can be understood by considering the total capillary force of the meniscus between the pillar top and the SU-8 disk at the sensor tip as consisting of two components: a force term due to the pressure difference between the inside and the outside of the curved meniscus i.e. the Laplace pressure, and a force term due to surface tension acting on the circumference of the meniscus:
\[ F_C = F_L + F_T = \gamma_{LG} \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \pi r^2 + 2 \pi r \gamma_{LG} \sin \theta_E \]  

where \( r \) is radius of the contact area, \( \gamma_{LG} \) is the surface tension of water, and \( R_1 \) and \( R_2 \) are the principal radii of curvature of the meniscus. For hydrophilic surfaces (\( \theta_c < 90^\circ \)), both the force due to Laplace pressure and the surface tension force are attractive forces that increase with the contact radius. For hydrophobic surfaces (\( \theta_c > 90^\circ \)), the force due to Laplace pressure is repulsive while the surface tension force remains attractive.

The capillary force can be simulated numerically using Surface Evolver [32]. In Surface Evolver, a mesh of triangles approximating the meniscus surface is evolved toward minimal energy by taking steps proportional to the negative of the gradient, under the constraint of constant volume and fixed contact radius at the sensor tip end of the meniscus. The computation yields the capillary force as a function of distance between the probed surface and the disk holding the droplet. In the case of hydrophilic micropillars, an additional constraint on the droplet contact radius on the pillar top can be applied; simulation results on the pillars are included in Fig. 6. Experimental force-distance curve from a single micropillar measurement (distance estimated from force-time data with known stage velocities) is compared with simulation in Fig. 7. For the case of flat surface, the simulated snap-in and pull-off forces as a function of cosine of the advancing and receding contact angles, respectively, are also plotted in Fig. 7.

Figure 7. Left: comparison of experimental force-distance curve and simulation, where the data is from a measurement on a single 10\( \mu \)m radius micropillar. Right: simulation of the snap-in and pull-off forces on a flat surface as a function of cosine of the advancing and receding contact angles, respectively (force normalized to surface tension and radius of the disk holding the droplet).

The capability of scanning droplet adhesion microscopy was first demonstrated by measuring forces on artificial surfaces. In the study by Samuel et al. [18], snap-in forces could not be measured for surfaces with equilibrium contact angles exceeding 145\(^\circ\) using a commercial force tensiometer. The custom built setup used in PUB3 has a microelectromechanical micro-force sensor with a resolution of 5nN - three orders of magnitude better than commercial instruments, allowing characterization of surfaces with very high contact angles. Various surfaces with contact angles in the 120\(^\circ\) – 170\(^\circ\) range were prepared to explore the upper limit for snap-in force measurement. Snap-in and pull-off forces on the surfaces are shown in Fig. 8, together with simulated forces.
The smallest measured snap-in force (mean value of three measurements) was 7.8 nN, on a surface with optically measured contact angles $\theta_A/\theta_R = 169^\circ/168^\circ$. The smallest measured pull-off force (mean value of five measurements) was 218.5 nN, on a surface with optically measured contact angles $\theta_A/\theta_R = 175^\circ/169^\circ$.

There seems not to be a contact angle limit beyond which the snap-in/pull-off force disappears. Therefore, using sensors with even better resolution should allow measuring snap-in and pull-off forces on surfaces with contact angles all the way up to $180^\circ$. It should be noted that the contact angles in Fig. 8 were determined as the mean value of ten measurements taken at ten different locations on each surface. The wide horizontal error bars for the contact angle values in Fig. 8 show how spatial variation of wetting properties diminish the meaning of even accurate contact angle measurements. Measured snap-in and pull-off forces, and contact angles for all the surfaces are listed in the supplementary materials document for PUB3, which is included in the appendix of the thesis.

Close to linear relation between pull-off force and cosine of $\theta_R$ has been reported [18], which agrees with the simulation in Fig. 7, and to some extent with the data in Fig. 8. However, the simulation disagrees with experimental data at the higher end of the contact angle range, especially for snap-in forces (see Fig. 6A and Fig. 8, left). As the simulation is based purely on surface energies, it does not account for any potentially significant effects with very high contact angles and small forces, such as electrostatic forces or contact line dynamics. The relation between snap-in force and $\theta_A$, and pull-off force and $\theta_R$, is thus left unclear for high contact angles. Nevertheless, it was shown in PUB3 that the snap-in force does not drop to zero for surfaces with $\theta_E$ higher than $\sim145^\circ$, as claimed by Samuel et al. [18].

Small differences in wetting forces can be detected using the method, as shown in Fig. 9. Line scan in 75 $\mu$m steps on a surface where repeated patterns have slightly different surface structure and contact angle (Fig. 9A,B) result in
consistently different pull-off forces (mean of three measurements) plotted in Fig. 9C. The method can also be used to map local variations of wetting properties on superhydrophobic natural surfaces. Area scan in 10μm steps over a region of interest on *Euploea tulliolus* (purple crow) butterfly wing (Fig. 9D,E) results in the snap-in and pull-off force maps shown in Fig. 9F, where one measurement was carried out on each of the black dots. The SEM micrographs in Fig. 9E show different dimensions and configurations of the scales in different parts of the wing, likely contributing to the variations in wetting forces.

Figure 9. Detecting local variations in wetting forces using scanning droplet adhesion microscopy. (A–C) Line scan over repeated patterns with slightly different wettability compared to the background show consistent difference in pull-off force (each data point in C is mean of three measurements, error bars denote standard deviation). (D–F) Area scan over a butterfly wing eyespot, where optically and topographically different surface structure is reflected in the corresponding wetting force maps (one measurement was carried out on each of the black dots). The wing was carefully fixed and flattened on a hard surface covered with a tacky film using tape.

Due to the discrete structure of the wing surface (Fig. 9E), often multiple steps were detected in the force as the droplet advanced or retracted to the next row of scales. The wing thus resembles an array of pillars, where wetting can proceed discretely from row to row. Regular pillar arrays are very commonly used as superhydrophobic substrates [54]–[61]. Water droplets have been shown to advance and retract in a step-like fashion on such surfaces [62]–[64]. These wetting steps happen by pinning (advancing) or depinning (retracting) from pillar to pillar, and they can be detected in the droplet adhesion force. Detection of wetting steps on a pillar surface (5μm pillar radius, 70μm spacing) is shown in Fig. 10. A water droplet first advancing and then receding on the pillar array (Fig. 10A) resulted in a force curve with multiple pinning/depinning steps (Fig. 10B) ranging from 20 to 60nN for pinning steps, and from hundreds of nN to
Wettability of surfaces

more than 10μN for depinning steps (Fig. 10C). Details of some of the wetting steps are shown in Fig. 10D. The number of touched pillars can be estimated from the number of wetting steps in the force curve.

The method developed in PUB3 covers a previously unreachable force range for wettability measurements with high resolution. Other force-based techniques used to measure surface adhesion and wetting properties include atomic force microscopy (AFM) at the lower end of forces (sub-nN range), and tensiometers for larger forces (μN range). Atomic force microscopy has been employed to measure interaction forces between surfaces and droplets of various liquids [65]–[68]. However, the AFM tip is quite limited in what materials may be put on it. Commercial tensiometers, on the other hand, offer force measurements only down to 1μN [69]. The scanning droplet adhesion microscopy technique of PUB3 fills the gap between AFM and tensiometers, providing accurate and automated force measurements in the 20nN – 1mN range. Spatial resolution down to 10μm was demonstrated in PUB3 on a butterfly wing that has a very irregular surface shape; even better resolution is expected on flat superhydrophobic surfaces that have higher contact angles.

One of the key questions about superhydrophobic surfaces is how homogeneous they are in terms of adhesion and wetting properties. It is quite common to give only one value for the static, advancing and receding contact angles of a surface, while in reality these can greatly vary from spot to spot. These variations are difficult to detect with optical methods, which also have problems reliably measuring very high contact angles and uneven, curved
surfaces. Therefore, normal force based measurement is an attractive complementary approach for superhydrophobic surface characterization.

The wetting force maps on the butterfly wing presented in Fig. 5 and Fig. 9 give a point-by-point indication of the local force variations. It would be interesting to connect them to the concept of the work of adhesion. This would require knowing the length scale over which the surface is probed during droplet contact. While the contact radius is known in the case of probing individual hydrophilic pillars, it is much harder to determine on an uneven surface such as the butterfly wing (see Fig. 4). Even on a flat (although rough) superhydrophobic surface, such as the black silicon surface used for the line scans in Fig. 9A, observing the small contact radius was not possible with the optics of the experimental setup. However, this is something that can be improved in the future.

As the method described above was developed after the other work reported in this thesis, it is not applied in the following Chapters 3 and 4, where the conventional advancing and receding contact angles are used to quantify surface wettability.
Wettability of surfaces
A plethora of techniques exist today for tuning the wettability of surfaces, varying from dry etching and wet chemical processes to energetic beam based methods and nanocoatings. Besides global wettability modification techniques, the ability to create well-defined microscopic wetting patterns has gained increasing importance during the past few years. Applications for such patterns are found in physical, chemical, as well as in biological systems. A few examples would be patterned liquid geometries for surface microfluidics, droplet microarrays for chemical synthesis and screening, and controlling the adhesion of proteins, cells, or bacteria.

In this chapter, the two approaches to tuning wettability are discussed: topographical and chemical modification. Two new methods utilizing each approach are presented. High-precision, spatial wettability patterning is discussed at the end of the chapter. Both of the new methods can be used for accurate spatial patterning.

### 3.1 Topographical modification

Wettability of a surface can be altered by modifying the surface topography. As discussed in Chapter 2, adding roughness to the surface increases the contact angle if the initial apparent contact angle is greater than 90°, and decreases it for angles smaller than 90°. The roughness can be random, or consist of well-defined geometrical shapes.

Random roughness has been produced on a wide variety of materials using e.g. laser machining [70], reactive ion etching (RIE) [71], wet chemical etching [72], and various deposition processes [73]–[76]. A typical example of random roughness is black silicon, or silicon nanograss, which is produced by anisotropic reactive ion etching. Black silicon has been widely employed in wetting applications during the past decade [77]–[82]. In PUB2, superhydrophilic and superhydrophobic areas on the same substrate were achieved using the random roughness of black silicon, shown in Fig. 11.
Fine geometrical control of the surface features is required for fabrication of surfaces that repel or confine low surface tension liquids, such as oils. One prominent technique is the use of sharp edges to confine highly wetting liquids. The basis of the principle is a simple geometrical rule, derived by Gibbs [83] describing the possible range of contact angles when a liquid front meets a mathematically sharp edge:

\[ \theta_0 \leq \theta \leq (180^\circ - \varphi) + \theta_0 \]  

(7)

where \( \theta \) is the apparent contact angle at the edge, \( \theta_0 \) is the (Young’s) contact angle of the liquid on the surface, and \( \varphi \) is the angle of the edge through the solid. This relation, known as Gibbs’ inequality, is illustrated in Fig. 12.

If the edge angle \( \varphi \) in Eq. (7) is smaller than 90°, the edge is said to be re-entrant, or undercut. In the extreme case \( \varphi = 0^\circ \), the upper limit for the apparent contact angle becomes 180° or more, theoretically stopping any liquid at the edge regardless of the equilibrium contact angle on the surface. Pillars with re-entrant edges have been employed by Tuteja et al. [21] and later by Liu et al. [84] to construct surfaces that repel all liquids. In PUB1, undercut edges were used for the first time to directly confine and guide low surface tension liquids in shapes ranging from micro to macroscale. The patterns were created on a silicon wafer coated with silicon oxide. The structure of the edge and contact angle of a cured adhesive droplet on an undercut ring shape are shown in the SEM micrographs of Fig. 13.
Figure 13. Undercut edges for pinning liquids. SEM micrographs of a 100μm diameter circular pad with undercut (left) and thermally cured low surface tension adhesive on the pad (right).

Repetition of the undercut edges, e.g. concentrically in the case of circles, makes it possible to adapt to different liquid volumes. The patterns confining and guiding liquids in PUB1 varied from micro- to macroscale (Fig. 14, top row), where the largest pattern consisted of paths covering the whole surface of a 10mm silicon wafer (Fig. 14, bottom row). Undercut edges were also utilized in PUB3, where silicon pillars had undercut silicon dioxide top, preventing overflow down the sidewall of the pillar. As the principle of the sharp edges is a purely topographical one, it should work with a wide range of materials where edges can be fabricated.

Figure 14. Low surface tension liquid confinement using various undercut structures.

Even though the undercut edge is ideal for pinning any liquids, a 90-degree edge angle is already enough for higher surface tension liquids, such as water. An edge height down to 1μm has been shown by Chang et al. [85] to reliably pin water. Furthermore, undercut edges may be difficult or impossible to realize if the area that confines the liquid is a functional component, such as a semiconductor die. In PUB4, pulsed laser beam processing was employed to mill trenches around square patterns, resulting in 90° edges. The edges were necessary for confining adhesives in surface tension-driven self-alignment of microchips. In PUB6, the edges of ultra-thin (10μm) square silicon dies were used to confine water on them for surface tension-driven self-alignment. An SEM micrograph of the die edges is shown in Fig. 15.
3.2 Chemical modification

The other approach to altering wettability of a surface is by chemical modification. High surface energy treatments tend to increase wettability of the solid surface by all liquids, while lowering the surface energy generally reduces wettability. Selecting a suitable surface chemistry depends on the substrate material and the liquid to be used. In the following the focus will be on water on various materials, as water is one of the most interesting and relevant liquids for a wide range of wetting applications.

Water is a polar liquid, i.e. water molecules have a net dipole moment, due to the oxygen atom in the molecule being more electronegative than the hydrogen atoms. The oxygen end of the molecule has a small negative charge while the hydrogen ends have a positive charge. Water mixes with other polar liquids, such as alcohols and glycols, but does not mix with non-polar liquids, such as oils and alkanes. Similarly, polar termination of chemical compounds on a surface attract water, while non-polar molecules repel water. A typical approach to increase hydrophilicity is to apply plasma treatments that create polar functionalities on the surface, e.g. –OH groups. Another way is to coat the surface with some metal, e.g. gold or aluminum, because metals are generally hydrophilic. For hydrophobic surface treatments, fluorine or chlorine containing polymer coatings are commonly used, e.g. Teflon-like fluoropolymers that contain non-polar functionalities.

In PUB7, flat hydrophilic/hydrophobic patterns were achieved by chemical patterning on a silicon surface. The hydrophilic sites were created by a thin (20nm) aluminum coating, while the hydrophobic background was due to a CHF3 fluoropolymer coating. Equilibrium contact angles on the hydrophilic patterns and on the background were 30° and 90°, respectively, as shown in Fig. 16.
The equilibrium contact angle on the hydrophobic background (90°) in Fig. 16 is not particularly high. It is not possible to achieve very high contact angles on a flat surface by chemical modification alone. Water contact angles of only up to around 130° can be achieved on flat surfaces. A combination of topographical and chemical modification is required for extremely high contact angles. As discussed in Chapter 2, surface roughness amplifies hydrophilicity/hydrophobicity. The black silicon “nanograss” surface presented in Fig. 11 provides enough roughness for extremely high and low contact angles. In PUB2, the black silicon surface was coated with 200nm of parylene-C, which is a chlorine containing variant in the parylene family of polymers. The chemical structure of parylene-C is depicted in Fig. 17. Chlorine in the benzene ring is a hydrophobic functionality in parylene-C. Fluorine was added to the structure in SF₆ plasma treatment to further increase hydrophobicity. The advancing and receding contact angles on the rough, coated and fluorinated black silicon were 162° and 134°, respectively.

Figure 17. Chemical formula of the polymer parylene-C used as a coating on black silicon in PUB2.

In PUB2, the chemistry of this surface was modified with electron beam induced local plasma while the topography remained unchanged, as verified by AFM. Chemical changes were characterized using X-ray photoelectron spectroscopy (XPS). The wide spectrum XPS data with high resolution insets are shown in Fig. 18a. An AFM scan over the edge of the modified area is shown in Fig. 18b, where no change in surface topography can be observed.
The high resolution insets in Fig. 18 reveal two changes in the surface chemistry: nitrogen (N1s peak) has appeared on the modified areas, and chlorine (Cl2p) has taken another form on the modified areas. The higher peak in the Cl2p region (200eV) represents a chlorine compound containing oxygen and/or fluorine. The new, lower peak (197.5eV) represents organic chlorine without oxygen or fluorine neighbors. The binding energies of the N1s peak (401eV) and the new compound in chlorine Cl2p peak (197.5eV) agree with values reported for polymers containing ammonium chloride functionalities [86], which are polar and hydrophilic. The XPS results also showed that fluorine content was reduced on the modified areas, as shown in Table 2. The reference values for the atomic concentrations in the table are slightly different because separate samples were used for each dose. As the initial superhydrophobicity of the surface can be attributed to the combination of surface roughness and fluorination of the parylene-C coating, removing part of the fluorine also reduces hydrophobicity. Together these two effects render the originally superhydrophobic surface hydrophilic, which is amplified by surface roughness.
Wettability modification and patterning

After modification, the advancing and receding contact angles on the surface were reduced to 10° and 0°, respectively.

The new chlorine and nitrogen containing functionality on the modified areas is chemically stable enough so that the surface remains superhydrophilic for a long time when stored in ambient air. No change in contact angles were observed 21 months after treatment. The good persistency offers an advantage over the commonly used oxygen, hydrogen and air plasma treatments, which can render a surface (super)hydrophilic, but the effect is usually short, lasting from hours to a few days.

3.3 High-precision wettability patterning

A multitude of methods for various materials exist for modifying global wetting properties of surfaces. However, spatial wetting patterns i.e. well-defined areas with distinct wetting properties are required in many applications. It is usually desirable that the wetting contrast between the patterned areas and the background is as high as possible. At the same time, the patterning techniques should be flexible in terms of pattern shape and size, and provide high resolution. For example, micro- and nanopatterns with high wetting contrast for water have been reported on both natural [87], [88] and synthetic [89], [90] surfaces. Such patterns have appeared in diverse applications including water collection from humid air mimicking desert beetles [1]; enhancing boiling heat transfer [91]; microelectromechanical systems assembly using surface tension-driven self-alignment [92]; arranging nanostructures in ordered arrays [93] for nanophotonic devices, e.g., antennas, filters, and optical processing circuits [94], transport of droplets for lab-on-a-chip devices [95]; and solving cross-contamination and cell migration problems in ultrahigh-density living cell microarrays [96].

A very common method for micropatterning is conventional photolithography, where a photosensitive layer is applied on the substrate and then selectively exposed to UV-light through a mask to transfer patterns on the mask to the substrate. In PUB1 and PUB5, photolithography was used in a simple fabrication process to realize micro- and macroscale wetting patterns.

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<th>$F, 1s$</th>
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<td>12.4%</td>
<td>6.6%</td>
<td>3.1%</td>
<td>1.6%</td>
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<tr>
<td>Reference</td>
<td></td>
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<td>Treated area</td>
<td></td>
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<tr>
<td>(0.7 mC cm$^{-2}$)</td>
<td>54.7%</td>
<td>17.5%</td>
<td>18.1%</td>
<td>6.1%</td>
<td>2.6%</td>
<td>1.0%</td>
</tr>
<tr>
<td>Reference</td>
<td></td>
<td></td>
<td></td>
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Table 2. Atomic concentrations (in atomic %) of elements on e-beam treated areas and non-treated reference areas, based on wide spectrum XPS survey
defined by undercut edges. Starting from thermally oxidized silicon wafer, photolithography and anisotropic dry etching were used to pattern the oxide, followed by isotropic dry etching of silicon for the undercut. The simple fabrication process is depicted in Fig. 19. Photolithography was also used to produce the hydrophilic-hydrophobic patterns in PUB7, where deposition of the fluoropolymer background on a clean silicon wafer was followed by lithographic definition and then sputtering of the hydrophilic patterns made of aluminum.

![Figure 19. Microfabrication of undercut edges. (a) Patterning of silicon dioxide on a silicon wafer using photolithography. (b) Anisotropic etching of silicon dioxide. (c) Photoresist removal. (d) Isotropic etching of silicon.](image)

While photolithography is a powerful tool for patterning, it has its drawbacks. Creating sub-μm features requires expensive equipment, and the wet processing steps involved may damage the often delicate surface structure of superhydrophobic substrates required for high wetting contrast. The surface may also be incompatible with photoresists and the related processing. Another technique for micro- and nanopatterning of superhydrophobic surfaces is microcontact printing [97], where stamping is used to transfer the patterns, but this process is also challenging to apply on rough surfaces [98].

To overcome the challenge of patterning rough, superhydrophobic surfaces, maskless methods based on energetic beams can be applied. Examples include laser interference lithography [99], pulsed laser beams [100], near-field scanning optical microscopy (NSOM) [101], and electron beam lithography (EBL) [102]; however, these techniques also have their limitations. Laser interference lithography can only produce features in the shape of a few types of interference patterns; pulsed laser beams have a resolution of few micrometers, limited by the beam spot size; and specific, photo or electron sensitive materials are required for NSOM and EBL.

One potential maskless solution is direct electron beam writing, where the beam modifies the surface directly without any pattern transferring layer or further processing steps. Effect of electron beams on surface wettability has been studied; e.g., high-energy electron beams (>500keV) can tune the wettability of poly(ethylene terephthalate) films [103] poly-l-lactic acid [104], rubber [105], and textile fabrics [106], where the maximum changes in water
contact angles varied from 15° to 32°; and low-energy electron beams (<0.5keV) [107], [108] can increase the water contact angle by 71° on a silicon dioxide surface, and by 25° on a zinc oxide nanomaterial. However, the electron beam was not controlled to produce wetting patterns in specific shapes on the surface in the aforementioned works.

In PUB2, a direct electron beam writing method for producing high wetting contrast patterns in an ESEM was reported. The substrate was initially superhydrophobic black silicon coated with fluorinated parylene-C. The electron beam ionizes water vapor and residual nitrogen in the chamber, creating a local plasma that interacts with the sample surface and renders it superhydrophilic. The concept is depicted in Fig. 20.

![Figure 20. Concept of high-resolution water wettability patterning using and electron beam in ESEM.](image)

The electron beam writing method is programmable as the beam or the sample stage motions can be controlled to create any 2D patterns. A variety of different patterns ranging from micrometers to millimeters in size were demonstrated, as shown in Fig. 21. The smallest linewidth achieved was around 1μm, with some sub-μm segments visible (Fig. 21d). For the used substrate, the smallest feature size i.e. the black silicon spikes set the limit for line resolution, but the beam itself should allow even smaller linewidths.

The effect of treatment parameters on the wettability change was studied. The key parameters include dose, water vapor pressure in the chamber, acceleration voltage and working distance. The best combination for the treatment was found to be an acceleration voltage of 30kV, a working distance of 4.5mm, a chamber pressure of 625Pa, a beam current of 5nA and a dose of 2.5mC cm⁻². Dose had the most significant role out of the studied parameters. It is given by the product of the beam current and the exposure time, in Coulomb per unit area. The study showed that the minimum dose required to induce the full superhydrophobic-to-superhydrophilic transition was 2.5mC cm⁻². However, lower doses already induce various degrees of reduction in the advancing and receding contact angles, as shown in Table 3.
Wettability modification and patterning

Figure 21. Wetting patterns written in ESEM. (a-c) Optical microscope images of water condensation in ambient air on various patterns consisting of linelike features. Scale bars 50μm. (d) Inverted optical microscope image of ten lines written with decreasing dose from top to bottom. Scale bar 10μm.

Table 3. Advancing and receding contact angles for areas treated in ESEM as a function of dose, where 100% corresponds to the minimum dose (2.5mC cm⁻²) required to induce superhydrophilicity.

<table>
<thead>
<tr>
<th>Dose (%)</th>
<th>Advancing CA</th>
<th>Receding CA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%</td>
<td>162°</td>
<td>134°</td>
</tr>
<tr>
<td>5%</td>
<td>162°</td>
<td>120°</td>
</tr>
<tr>
<td>10%</td>
<td>143°</td>
<td>77°</td>
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<tr>
<td>30%</td>
<td>128°</td>
<td>64°</td>
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<tr>
<td>65%</td>
<td>122°</td>
<td>54°</td>
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<td>85%</td>
<td>27°</td>
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<td>95%</td>
<td>25°</td>
<td>&lt; 10°</td>
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<tr>
<td>100%</td>
<td>&lt; 10°</td>
<td>~ 0°</td>
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</table>

Methods to produce wettability gradients on surfaces have been actively pursued in recent decades. Common applications for wettability gradients are in cell and protein interaction studies [109], [110] and spontaneous motion of droplets on a surface [111]–[113]. The methods to create wettability gradients vary from radio frequency plasma discharge [114], corona discharge [115], liquid [116] and vapor diffusion [111], [117] to pulsed laser treatments [100], ion exchange interactions [118] and electrochemical corrosion [119]. The dose dependency of the contact angles in the electron beam writing method of PUB2 (Table 3) also allows creating wettability gradients. Linear variation of scanning time over a distance of 1.9mm in steps of 100μm resulted in the wettability gradient shown in Fig. 22.
In summary, increasing the electron beam dose leads to a stronger (more hydrophilicity) effect and vice versa; increasing the water vapor pressure and thus the relative humidity in the ESEM chamber leads to a stronger effect, especially after a critical threshold between 85% and 92% relative humidity; higher acceleration voltage for a given working distance leads to a stronger effect as the electron beam has more energy for interactions at the sample surface; and working distance has little influence on the resulting contact angles, but smaller working distance leads to better definition of the produced patterns.

The study in PUB2 was focused on black silicon coated with fluorinated parylene-C. However, the wettability change was observed also on other materials, including silicon dioxide, black silicon coated with a fluoropolymer and thermally hydrocarbonized porous silicon (THCPSi). On each material, a similar, increasing hydrophilicity effect was obtained as a result of the electron beam treatment. The effects can be seen in Fig. 23, where condensation in ambient air on the different materials reveal modified wetting properties.
Today, ESEM is an established tool for micro- and nanoscale wetting studies. The capability of having liquid water in the chamber while imaging at high resolution is attractive for such studies. ESEM has been used, e.g., to observe the wetting dynamics of evaporation-condensation on superhydrophobic surfaces [56], [120], the fine structure of the triple line and Cassie-Wenzel transitions [121], growth and shedding of condensing droplets [122], microdroplet growth mechanism during water condensation on superhydrophobic surfaces [123], and multidrop coalescence effects during condensation on superhydrophobic surfaces [124]. The results of PUB2 show that the electron beam may affect the materials that are used in wetting studies during imaging in ESEM, possibly leading to distorted results. On the other hand, being aware of the electron beam effects may lead to new techniques in micro- and nanoscale wetting studies.
4. Surface tension-driven self-alignment

Micro- and nanoassembly is a key enabling technology for the integration of complex microsystems. One of the most pronounced technologies to achieve high throughput and high precision simultaneously is self-assembly. Self-assembly of microparts can be implemented through the self-alignment process, which uses the principle of minimum potential energy, where the gradient of potential is designed to drive the parts toward desired locations. Self-alignment can be implemented using different principles such as shape recognition [125]–[132], capillary forces [133]–[136] magnetic force [137] and electrostatic force [138]. Impressive results have been claimed, e.g., 62,500 chips assembled in 45 s with submicrometer precision [133].

In capillary force based self-alignment of micro- and nanoparticles, surface tension of a liquid droplet between a part and a matching pattern on the substrate aligns the part and the pattern as the droplet minimizes its surface energy. Such surface tension-driven self-alignment has been combined with robotic microhandling into a hybrid microassembly strategy [92], [136], [139]–[141], where coarse robotic pick-and-place is complemented with high-accuracy self-alignment. This approach is especially attractive for the assembly of sub-millimeter components such as integrated circuit (IC) dies, due to the high accuracy and potentially very fast robotic handling. The concept of surface tension-driven droplet self-alignment is depicted in Fig. 24, with images of a real experiment.

The liquid used in surface tension-driven self-alignment can be freely chosen, but it must be confined within the pattern on the substrate during the whole process. Overflow at the pattern edge often leads to unrecoverable alignment failure, especially with liquids other than water, which cannot be easily removed.

Figure 24. The concept of surface tension-driven droplet self-alignment. (a-f) Surface tension of a liquid droplet aligns a micropart on a matching pattern. (g) Optical microscope images of a real experiment. © 2010 IEEE.
Surface tension-driven self-alignment

or leave residue.

In PUB5, the undercut edges developed in PUB1 were shown to provide robust and reliable confinement for droplet self-alignment using a low surface tension ($\gamma = 34 \text{mN m}^{-1}$) adhesive. The $200 \times 200 \mu\text{m}^2$ square receptor sites were fabricated following the procedure shown in Fig. 19. Microparts of matching size were prepared out of SU-8 photoresist. The assembly process follows the one shown in Fig. 24, ending in the part aligned on the receptor site, with a layer of adhesive between them. The assembly was then placed in a convection oven to cure the adhesive for SEM imaging. SEM micrographs of the receptor site and the aligned micropart on top of it are shown in Fig. 25, where sub-μm accuracy of the alignment can be seen.

![Figure 25. Result of surface tension-driven self-alignment of a micropart on a $200 \times 200 \mu\text{m}^2$ receptor site with undercut edges. The liquid between the part and the receptor site is a low surface tension ($\gamma = 34 \text{mN m}^{-1}$) adhesive in cured state.](image)

Due to the pinning capability of the receptor site undercut edges in PUB5, the micropart could be dragged almost completely outside the outline of the receptor site before releasing it (Fig. 26, left). Furthermore, during the alignment the adhesive between the part and the receptor site wet the bottom surface of the SU-8 part even outside the receptor site edges without overflow (Fig. 26, right). The result is improved reliability and robustness of hybrid microassembly as the undercut edges prohibit liquid overflow even with extreme misalignment of the micropart before release.
Figure 26. Optical microscope images of surface tension-driven self-alignment with adhesive on a 200 × 200 μm² receptor site with undercut edges. Left: sideview of extreme misalignment before release of micropart. Right: topview images of the self-alignment after release.

Hybrid microassembly can also be applied to stacking of ultra-thin dies, where the liquid confinement is achieved by 90° edges of the dies themselves. Ultra-thin dies are thinned semiconductor chips with low thickness values below e.g. 20μm, which is an evolving value as the fabrication technologies progress. Techniques for the fabrication and assembly of ultra-thin dies are primarily needed in 3D integration of semiconductor dies, where different active dies are vertically connected using through-silicon-vias (TSV). Ultra-thin dies offer many benefits for integrated circuit (IC) assemblies, including reduced package height, enhanced heat flow, faster operation due to shorter interconnects, and easier TSV formation due to the reduced thickness.

Good alignment of TSVs in a 3D ultra-thin die stack is crucial for operation of the assembly. The required alignment accuracy is approaching the sub-μm level, and the number of aligned layers in the stack is growing beyond two [142]. Achieving sub-μm alignment, which translates to yield, while maintaining high throughput, is challenging for commercial die bonders that rely on machine vision for the alignment. Fragility and flexibility of ultra-thin dies makes the task even more demanding.

In PUB6, robotic pick-and-place was combined with surface tension-driven self-alignment for stacking square 1 x 1mm² ultra-thin (10μm) dies. The pick-and-place tool was a vacuum gripper with a soft gripping head for safe handling of the dies. Water was used as liquid in the self-alignment. The water droplet should be confined by the edges of the previous die in the stack for the alignment to work. The 90° edges of the dies provide enough confinement, as discussed in Chapter 3.1. For water to go over the edge, it should have a contact angle of 90° + θ₀ (Eq. (7)) with respect to the top surface of the die, where θ₀ is the natural contact angle of water on the die (~10°). Such a high contact angle would require either a huge volume of water on the die or serious defects on the die edges that allow wetting to proceed down the sidewall of the die. It is therefore very likely that water is pinned on the edge. However, there is a cavity used in ultra-thin die release [143], near one edge (Fig. 27a), and the cavity also has a 90° edge. These kind of features can pin the self-alignment liquid instead of the desired outer edges of the die, leading to alignment problems. Three strategies were tested in the droplet deposition,
shown in Fig. 27. If a medium sized droplet was deposited in the center of the bottom die, water was pinned by the cavity edge, leading to significant misalignment as the added die then aligned along the edge of the cavity (Fig. 27b). Deposition of one large droplet that covered the entire bottom die (Fig. 27c) eliminated the alignment error as the added die aligned according to the edges of the bottom die, but the drawback was a long evaporation time around 90s. The third approach was to deposit four small droplets in each corner of the bottom die (Fig. 27e), avoiding the cavity. This resulted in good alignment, with significant reduction of evaporation time down to 1 second. Assembly of a 2-die stack on another to form a 4-die stack of ultra-thin dies is shown in Fig. 27g, where the four water droplets in each corner of the bottom stack can be seen. A stack of up to 12 dies was assembled with sub-μm accuracy.

**Figure 27.** Droplet deposition strategies in surface tension-driven self-alignment of ultra-thin (10μm) dies into a stack (a-f); and sideview of the alignment of a 2-die stack onto another (g). Water droplets were shot from a distance using a non-contact piezoelectric micro-dispenser.

In the work described above, hybrid microassembly was tested with well-defined microparts and receptor sites. However, in real world applications the microparts and receptor sites are often not perfectly defined due to low cost and high throughput fabrication processes. For example, a real radio frequency identification (RFID) antenna can have wavy or jagged edges (Fig. 28, left).

The question of how these irregularities affect surface tension-driven self-alignment was addressed in PUB7. The receptor sites were 200 × 200 μm² flat, chemical patterns that were deliberately designed to have irregular edges in various degrees. The irregularities varied from constant spikiness to random jaggedness (Fig. 28, right). Optical micrographs of some of the fabricated patterns are shown in Fig. 28. The patterns are sputtered 20nm thick aluminum while the background is a Teflon-like polymer grown in a reactive ion etching process, with equilibrium water contact angles of 30° and 90°, respectively. Patterns were defined using photolithography. The 20nm edge height of the aluminum is not enough to geometrically pin water [85]. Therefore, the wetting contrast can be fully attributed to surface chemistry. The 60° contact angle contrast between the patterns and the background is enough to reliably confine water on the patterns during self-alignment. The microparts aligned on the patterns were made of SU-8, with 200 × 200 μm² area and 50μm thickness.
The parameters varied in the pattern edge design were amplitude and pitch of the irregularities. Two types of edge jaggedness were created: constant pitch / constant amplitude zigzag spikes; and constant pitch / random amplitude jaggedness, where the amplitude followed normal distribution with a pre-defined standard deviation. Other parameters, such as droplet volume, and releasing position of the micropart, were fixed in the experiments. The results show that self-alignment can provide high accuracy even on flat chemical patterns with irregular edges, both for constant spikiness and random jaggedness.

A step further towards real-world applications of surface tension-driven self-alignment, and hybrid microassembly, was taken in PUB4. The paper summarizes results of an EU FP7 project FAB2ASM, where surface tension-driven self-alignment played a key role in microsystem integration of real, functional dies. Droplet self-alignment was applied in three applications: i) integration of microchips on lead-frame, ii) integration of vertical cavity surface emitting lasers (VCSEL) on optical benches, and iii) 3D integration of thin dies connected with TSVs.

In the first application, 300 × 300 μm² microchips were aligned and fixed to lead-frames using hybrid microassembly, where the pick-and-place speed of a state-of-the-art die bonding machine (> 40k units per hour) was combined with the high accuracy of surface tension-driven self-alignment. The lead-frame is copper with a nickel-palladium-gold (NiPdAu) finish on top. Receptor sites were fabricated by chemically etching 150μm wide trenches around squares matching the die size. Following the geometrical confinement principle of PUB1, the etching process was fine-tuned to create a slight undercut at the edges of the pattern (Fig. 29, left). The undercut was necessary, because the thermally curable adhesives used in the self-alignment have low surface tensions (γ < 35mN m⁻¹). Droplets of the adhesive with a suitable volume were dispensed on the receptor sites (Fig. 29, right) at the same high speed as the pick-and-place of dies afterwards. Each droplet was inspected right after dispensing by machine vision.
Figure 29. Undercut edge pattern etched on a lead frame used in industrial microassembly processes (left); droplet of adhesive deposited on the pattern (right).

In the pick-and-place of microchips on the undercut receptor sites, a placement error of $75\mu m$ in x-direction was imposed to see the accuracy of self-alignment. Functional microchips after self-alignment on the lead-frame are shown in Fig. 30. The alignment accuracy in x-direction was observed to be $\sim 2\mu m$ ($\sigma$). However, this error includes misalignment of the receptor site locations on the lead-frame, and does not therefore reflect the die-to-pattern alignment accuracy, which is close to $1\mu m$. Moreover, the microchips were diced in a standard process that has an accuracy of $1.5\mu m$ ($\sigma$), and the etching of the receptor sites on the lead-frame is limited by resolution of photolithography. Even so, the achieved $\sim 2\mu m$ global alignment accuracy was already a great improvement for an industrial process with $> 40k$ part placements per hour [144].

Figure 30. Functional microchips aligned on a lead frame using surface tension-driven self-alignment.

In the second application described in PUB4, vertical cavity surface emitting lasers (VCSEL) were integrated on optical silicon benches. Two sizes for individual VCSELs were used, $250 \times 250 \mu m^2$, and $125 \times 125 \mu m^2$. However, the industrial applications of VCSELs are related to optical data transmission, thus requiring an array format. A picture of a $1 \times 4$ array of $125 \times 125 \mu m^2$ VCSELs is shown in Fig. 31a. The silicon platform serving as an optical bench for characterization of the VCSEL performance is shown in Fig. 31b. The area surrounding the receptor site for the VCSEL array was chemically functionalized to be hydrophobic, leading to confinement of droplets deposited on the receptor site. Robotic pick-and-place and water droplet self-alignment was used to align the array, followed by solder reflow to bind the solder bumps on the silicon bench to contact pads on the VCSEL array. The hydrophobic background and the solder bump edges confined water during the initial droplet self-alignment, whereas the meniscus of liquefied solder between the bumps and the contact pads ensured final alignment during reflow heating.
An assembled array is shown in Fig. 31c. Alignment of the arrays were checked against reference features (optical apertures) on the receptor site. The electro-optical characteristics (Light-Current-Voltage) as well as thermal behavior of the assembled devices were tested. The results showed that the VCSELs remained fully functional after the assembly, and that the thermal characteristics (wavelength-temperature variation coefficient) was within the range of typical values for this type of VCSEL. Therefore, the results show promise for the application of surface tension-driven self-alignment to the assembly of optoelectronic devices.

The final application described in PUB4 was 3D integration i.e. stacking of thin (50μm) semiconductor dies, where TSVs between any two dies in the stack must be accurately aligned for the assembly to work. Schematic of the targeted three-layer stack (not to scale) is shown in Fig. 32. The TSVs are 5μm in diameter, with 20μm center-to-center distance. Slow, robotic, machine vision based die-to-die alignment was replaced with surface tension-driven self-alignment, followed by thermal bonding at 250°C to melt and join the solder bumps connecting TSVs between layers of the stack. A liquid droplet deposited on the lower die was confined either due to chemical functionalization (for the bottommost layer), or edges of the die (for the middle layer). No misalignment of the dies could be observed under optical microscope after bonding (Fig. 32, middle). The achieved accuracy is below 2μm. SEM micrograph shows the structure of the connection TSVs between the layers (Fig. 32, right).
Figure 32. 3D integration of three layers of thin dies connected with TSVs. Schematic of a 3-layer stack (left); 3-layer stack aligned using surface tension-driven self-alignment (middle); SEM micrograph of a joined TSV connection (right).
5. Conclusions

Controlling wettability of surfaces is essential for a wide range of applications in science and technology, where the processes depending on tailored wetting properties vary from physical and chemical to biological and biomedical. Challenges arise when low surface tension liquids are used as they easily spread on all surfaces, and controlled wettability is often required in well-defined areas. A prominent type of surfaces with special wetting properties are superhydrophobic surfaces that can completely prevent wetting by water, which makes their characterization difficult for traditional wettability measurements.

This thesis reports new methods for characterization of superhydrophobic surfaces, controlling the spreading of low surface tension liquids, and precisely patterned wettability. In PUB3, a method based on normal force measurement was developed for characterization of superhydrophobic surfaces, where traditional optical contact angle measurements may not give accurate and reliable results. A sub-mm size water droplet attached to the end of a vertical microforce sensor is brought in contact with the surface, and the force during approach, contact, and retraction is recorded. The method, scanning droplet adhesion microscopy, can reveal small local variations of wetting and adhesion properties on a surface. The spatial resolution of the technique increases as the wettability of the surface decreases, because the contact area between the droplet and the surface depends on the wettability. Down to 10μm spatial resolution of wetting properties measurement was demonstrated on a superhydrophobic butterfly wing. Even though only water was used in PUB3, the measurement principle may be applied to other liquid-surface pairs. The accuracy of the method depends on the resolution of the force sensor, and can thus be increased in the future with better sensors.

Scanning droplet adhesion microscopy is a novel approach to characterization of superhydrophobic surfaces, as opposed to the traditional contact angle measurements. It provides high enough sensitivity and precision to probe the often delicate and sometimes uneven superhydrophobic surfaces, such as a butterfly wing. The method allows for the first time experimental access to microscale wetting heterogeneity of superhydrophobic surfaces, which affects macroscale wetting phenomena, such as condensation and sliding angle. Further development of the method includes studying the exact relationship between the measured droplet adhesion forces and the advancing/receding contact angles, and extending the technique to other liquids.
In PUB1, a simple geometrical feature – sharp edge – was shown to prohibit
the spreading of low surface tension liquids. Liquids can be pinned already by
e.g. 90° edges, but the extreme case where the edge angle approaches 0°, i.e. the
dge is undercut, provides more reliable pinning. The principle of sharp or
undercut edges were applied in PUB3-6 in diverse applications for liquid
confinement purposes. As a geometrical rule, the sharp edge works in principle
on any material and both at micro- and macroscales.

The undercut edge principle has great potential to become a universal method
in liquid confinement, regardless of surface tension. Apart from simple
confinement, it can be used to guide surface microflows of low surface tension
liquids, extending the applicability to surface microfluidics. The technique is
already been used in diverse applications, some of them outside the work
described in this thesis. Even though the principle is simple and easy to
demonstrate, quality of the undercut edge in different materials should be
studied and improved in the future, because it is critical to the reliability of the
method.

For accurate wettability patterning, a chemical modification method was
introduced in PUB2. The electron beam of an environmental scanning electron
microscope (ESEM) was used to make an initially superhydrophobic surface
superhydrophilic with sub-μm line resolution. The method is flexible because
no mask is needed, and the produced wetting patterns were shown to be
chemically stable, persisting for over a year. Although the patterns were
produced on a parylene-C coated black silicon substrate, similar wettability
change effects were observed on various other materials as well.

The patterning method provides high wetting contrast and high precision
simultaneously for water wettability patterning, which has not been achieved in
earlier work with electron beams. The results of PUB2 are also interesting for
micro- and nanoscale wetting studies in ESEM, where the beam may change the
wetting properties in situ. Understanding the effects of the electron beam on
various materials requires further studies, and more efforts should be put
towards using the method to create wettability gradients, which is an interesting
application of chemical patterning.

Finally, PUB4-7 demonstrated different applications of surface tension-driven
self-alignment, where confinement of liquid is crucial. Both geometrical
features and chemical functionalization were applied to control wetting in
diverse cases. Industrially relevant applications were reported in PUB4, where
the sharp edges developed in PUB1 were used to realize self-alignment in an
industrial, high-throughput microassembly process where adhesives of low
surface tension are involved. Self-alignment with suitable surface engineering
can thus be used to achieve high precision and reliability in demanding
assembly processes. It is expected to complement traditional machine vision
based assembly techniques in the future, especially in 3D integration of
heterogeneous components.
References


References


