

DISSERTATION

From Silicon Wafers to Silicon Nanowires: Chemical modification of 2D and 3D Silicon Surfaces

ausgeführt zum Zwecke der Erlangung des akademischen Grades eines

Doktors der Naturwissenschaften unter der Leitung von

Ao.Univ.Prof.Dipl.Ing.Dr. Helmuth Hoffmann

E163

Institute of Applied Synthetic Chemistry

eingereicht an der Technischen Universität Wien

Fakultät für Technische Chemie

von

M.Sc. Anders Henriksson Matr. Nr. 0825827 Mohsgasse 25/5, 1030 Wien

Wien, am 25 Juni 2012

Acknowledgement

During my graduate studies, I have enjoyed the opportunity to meet and work with numerous peoples.

First of all I thank Prof. Hoffmann, who gave me the opportunity to work in his group, introduced me to a new very interesting research field, for his support, for the many good advices and the pleasant and friendly atmosphere making my stay at Vienna University of Technology very easy and enjoyable.

I also thank Prof. Friedbacher for AFM and SEM measurements and for his advices and the good scientific collaboration. I thank Dr. Elisabeth Eitenberger for allways having time to measure my samples with SEM.

Further I thank Prof. Lugstein who introduced me to the topic of silicon nanowire, Dr. Ole Bethge for XPS measurements, DI. Johannes Greil for preparing silicon nanowire transistors, the laborants for always providing the chemicals I needed and finally my friends and colleagues for the support and good times.

Kurzfassung

Oxidfreie Siliziumsubstrate, funktionalisiert mit organischen Monoschichten, spielen heute eine Schlüsselrolle in verschiedenen Gebieten der Nanowissenschaften wie etwa in der Katalyse, der Sensorik oder der Nanoelektronik. Voraussetzung für praktische Anwendungen ist ein vielseitges und zuverlässiges Oberflächenmodifizierungsverfahren, welches die Beschichtung von Siliziumsubstraten mit organischen Monoschichten, ausgestattet mit bestimmten, gewünschten terminalen Funktionlitäten, mit bestmöglicher Kontrolle über Struktur und Reaktivität der modifizierten Oberflächen ermöglicht.

In der vorliegenden Dissertation wurden Siliziumsubstrate mit unterschiedlicher Topographie (Siliziumwafer, poröses Silizium und Silizium-Nanodrähte) hergestellt und mit organischen Monoschichten modifiziert, welche über bestimmte funktionale Endgruppen an der Grenzfläche Film/Umgebungsmedium verfügten. Verschiedene Modifizierungsstrategien wurden untersucht und verglichen, zum einen die präadsorptive Synthese von Adsorbaten mit den gewünschten terminalen Funktionalitäten und zu anderen Zwei-Stufen Prozesse, wo auf der Oberfläche zunächst eine Primärschicht adsorbiert wird welche anschließend mittels in-situ Oberflächenreaktionen die gewünschte Zusammensetzung erhält oder mit einer entprechend funktionalisierten Sekundärschicht gekuppelt wird. Die Oberflächenchemie und die resultierenden Monoschichteigenschaften wurden mit einerm Verbund verschiedener (Reflexions-Absorptions Oberflächenmodifizierungstechniken Infrarotspektroskopie, Ellipsometrie, Rasterelektronenmikroskopie und Kontaktwinkelmessungen) untersucht. Ein Vergleich zwischen den chemisch identischen, aber strukturell unterschiedlichen Siliziumsubstraten, die dem gleichen Modifizierungsprozess unterworfen wurden, ergab Unterschiede siginifikante in molekularen Eigenschaften wie Reaktivität und Oberflächenstruktur und makroskopischen Egenschaften wie Oberflächenbenetzbarkeit, welche auf die unterschiedliche Oberflächentopographie der Substrate zurückgeführt wurden. Stärken und Schwächen der verschiedenen Substrate und Oberflächenmodifizierungsverfahren wurden untersucht und gegenübergestellt mit dem Ziel; ein effizientes und praxistaugliches Protokoll zur Herstellung funktioneller Siliziumsubstrate zu entwickeln.

Abstract

Oxide-free silicon substrates, functionalized with organic monolayers, play a key role today in various fields of nanoscience including catalysis, sensor fabrication and nanoelectronics. Fundamental for practical applications is a versatile and reliable surface modification protocol, allowing organic monolayers with certain desired terminal functionalities to be attached to silicon substrates with a high level of control over the reactivity and structure of the modified surfaces.

In this thesis, silicon substrates with different topographies (silicon wafers, porous silicon, silicon nanowires) were prepared and subsequently functionalized with organic monolayers carrying specific terminal groups located at the monolayer/ambient interface. Different functionalization strategies were tested and compared, including pre-adsorption synthesis of adsorbates with the desired terminal functionalities, or a two-step approach where the surface is first primed with a precursor monolayer which is subsequently transformed by insitu surface reactions to the desired composition or coupled with a properly functionalized overlayer. The surface chemistry and the resulting monolayer properties of the adsorbate layers were investigated using a combination of different surface characterization methods such as reflection absorption infrared spectroscopy (RAIRS), ellipsometry, scanning electron microscopy (SEM) and contact angle measurements. A comparison between the chemically identical, but structurally different silicon substrates subjected to identical chemical modification procedures revealed profound differences in molecular properties (reactivity, surface structure) as well as in macroscopic properties like the surface wettability caused by the different surface topographies of the parent silicon substrates. Opportunities and limitations of the different substrates and surface modification approaches were explored, aiming at a versatile and reliable protocol for the preparation of functional silicon substrates that can be employed for future practical applications.

Publications resulting from this thesis

Henriksson, A., Friedbacher, G. & Hoffmann, H. Surface Modification of Silicon Nanowires via Copper-Free Click Chemistry. Langmuir (2011) 27 (12), pp 7345–7348

Henriksson, A & Hoffmann, H. Structure of Alkyne Monolayers on Hydrogen-Terminated Si(100) Surfaces Investigated by External Reflection Infrared Spectroscopy, Applied Spectroscopy, submitted

Henriksson, A., Friedbacher G. & Hoffmann, H., Wetting Properties of Flat and Structured Silicon Surfaces: Effect of Surface Morphology and Chemical Composition, in preparation

Abbreviations

AFM	Atomic force microscopy	
ATR	Attenuated Total Reflection	
СВ	Cassie-Baxter	
CVD	Chemical vapour deposition	
DDDP	1,2-Decadiol-dipropiolate	
DFT	Density-functional theory	
DMF	Dimethylformamide	
DMSO	Dimethyl sulfoxide	
DRIFT	Diffusion reflection fourier transform	
EDDP	1,2 Ethanediol-dipropiolate	
FET	Field effect transistor	
FTIR	Fourier transform infrared spectroscopy	
HER	Hydrogen evolution reaction	
LB	Langmuir-Blodgett	
MCT	Mercury cadmium telluride	
NMR	Nuclear magnetic resonance	
NP	Nanoparticle	
NW	Nanowire	
OTS	Octadecyltrichlorosilane	
OWRK	Owens-Wendt-Rabel-Kaeble	
PL	Photoluminescence	
PMMA	Poly(methyl methacrylate)	
RAIRS	Reflection absorption infrared spectroscopy	
RMS	Root-Mean-Square	
SAM	Self assembled monolayer	
SEM	Secondary electron microscopy	
SNR	Signal-to-noise ratio	
TMS	Tetramethylsilane	
XPS	X-ray photoelectron spectroscopy	
TDP	Tetradecanolpropiolate	
TGS	Triglycine sulphate	
TIR	Transmission infrared	
\/I S		
VL3	Vapour liquid solid	

Table of Content

1.1. Silicon Wafers 1 1.2. Porous Silicon 3 1.3. Silicon Nanowires 6 1.4. Functional Silicon surfaces based on Self Assembled Monolayers 10 1.4.1 Strategies and Applications 10 1.4.2. Organosilane monolayers on native, oxide-covered silicon 13 1.4.3. Si-C bonded monolayers on oxide free silicon 15 2. Characterization methods 20 2.1. Ellipsometry 22 2.2. Contact angle Measurements 23 2.3. Infrared spectroscopy 27 2.3.2. Determining surface orientation with RAIRS 30 3.4.3. Sitrate and materials 32 3.1. Chemicals and materials 32 3.1. Chemicals and materials 32 3.2. Substrate Preparation 35 3.3. Chemical modification of silicon substrates 36 3.4. Infrared spectroscopy measurements 39 3.5. Ellipsometric measurements 43 3.6. Contact Angle measurements 43 3.7. NMR measurements 43 3.6. Contact Angle measurements 44 4.1 Preparation and properties of oxide-free planar (2D) and structured (3D) silicon substrates 44 <th>1. Introduction</th> <th>1</th>	1. Introduction	1
1.2. Porous Silicon 3 1.3. Silicon Nanowires 6 1.4. Functional Silicon surfaces based on Self Assembled Monolayers 10 1.4.1. Strategies and Applications 10 1.4.2. Organosilane monolayers on native, oxide-covered silicon 13 1.4.3. Si-C bonded monolayers on native, oxide-covered silicon 13 1.4.3. Si-C bonded monolayers on vide free silicon 15 2. Characterization methods 20 2.1. Ellipsometry 22 2. Contact angle Measurements 23 2.3. Infrared spectroscopy 27 2.3.1. Reflection Absorption Infrared Spectroscopy (RAIRS) 27 2.3.2. Determining surface orientation with RAIRS 30 3. Experimental 32 3. Chemicals and materials 32 3. Chemicals and materials 32 3. Chemicals and materials 32 3. Contract Angle measurements 34 3.6. Contact Angle measurements 43 3.6. Contact Angle measurements 43 3.6. Contact Angle measurements 43 3.7. NMR measurements 43 3.6. Contact Angle measurements 44 4.1 Pre	1.1. Silicon Wafers	1
1.3. Silicon Nanowires 6 1.4. Functional Silicon surfaces based on Self Assembled Monolayers 10 1.4.1. Strategies and Applications 10 1.4.2. Organosilane monolayers on native, oxide-covered silicon 13 1.4.3. Si-C bonded monolayers on oxide free silicon 15 2. Characterization methods 20 2.1. Ellipsometry 22 2. Contact angle Measurements 23 2.3. Infrared spectroscopy 27 2.3.1. Reflection Absorption Infrared Spectroscopy (RAIRS) 27 2.3.2. Determining surface orientation with RAIRS 30 3.6 Experimental 32 3.1. Chemicals and materials 32 3.2. Substrate Preparation 35 3.3. Chemical modification of silicon substrates 36 3.4. Infrared spectroscopy measurements 39 3.5. Ellipsometric measurements 43 3.6. Contact Angle measurements 43 3.7. NMR measurements 43 3.6. Contact Angle measurements 43 3.7. NMR measurements 44 4.1 Preparation and properties of oxide-free planar (2D) and structured (3D) silicon substrates. 44 4.1.2. Porous silic	1.2. Porous Silicon	3
1.4. Functional Silicon surfaces based on Self Assembled Monolayers 10 1.4.1 Strategies and Applications 10 1.4.2. Organosilane monolayers on native, oxide-covered silicon 13 1.4.3. Si-C bonded monolayers on oxide free silicon 15 2. Characterization methods 20 2.1. Ellipsometry 22 2.2. Contact angle Measurements 23 2.3.1. Infrared spectroscopy 27 2.3.2. Determining surface orientation with RAIRS 30 3.5. Experimental 32 3.1. Chemicals and materials 32 3.2. Substrate Preparation 35 3.3. Chemical modification of silicon substrates 36 3.4. Infrared spectroscopy measurements 39 3.5. Ellipsometric measurements 43 3.6. Contact Angle measurements 43 3.7. NMR measurements 43 3.6. Contact Angle measurements 43 3.7. NMR measurements 43 4.1.1 Silicon Nanowires 44 4.1 Preparation and properties of oxide-free planar (2D) and structured (3D) silicon substrates 44 4.1.1 Silicon Nanowires 48 4.2. Alkylation of silicon surfaces via hydrosily	1.3. Silicon Nanowires	6
1.4.1 Strategies and Applications 10 1.4.2. Organosilane monolayers on native, oxide-covered silicon 13 1.4.3. Si-C bonded monolayers on oxide free silicon 15 2. Characterization methods 20 2.1. Ellipsometry 22 2.2. Contact angle Measurements 23 2.3. Infrared spectroscopy 27 2.3.1. Reflection Absorption Infrared Spectroscopy (RAIRS) 27 2.3.2. Determining surface orientation with RAIRS 30 3. Experimental 32 3.1. Chemicals and materials 32 3.2. Substrate Preparation 35 3.3. Chemical modification of silicon substrates 36 3.4. Infrared spectroscopy measurements 39 3.5. Ellipsometric measurements 43 3.6. Contact Angle measurements 43 3.7. NMR measurements 43 3.6. Contact Angle measurements 43 3.7. NMR measurements 43 4.1.1 Silicon 1000 wafers 44 4.1 Preparation and properties of oxide-free planar (2D) and structured (3D) silicon substrates 44 4.1.1 Silicon Nanowires 45 4.1.2. Porous silicon 47 <	1.4. Functional Silicon surfaces based on Self Assembled Monolayers	10
1.4.2. Organosilane monolayers on native, oxide-covered silicon 13 1.4.3. Si-C bonded monolayers on oxide free silicon 15 2. Characterization methods 20 2.1. Ellipsometry 22 2.2. Contact angle Measurements 23 2.3. Infrared spectroscopy 27 2.3.1. Reflection Absorption Infrared Spectroscopy (RAIRS) 27 2.3.2. Determining surface orientation with RAIRS 30 3. Experimental 32 3.1. Chemicals and materials 32 3.2. Substrate Preparation 35 3.3. Chemical modification of silicon substrates 36 3.4. Infrared spectroscopy measurements 39 3.5. Ellipsometric measurements 43 3.6. Contact Angle measurements 43 3.7. NMR measurements 43 4.1 Preparation and properties of oxide-free planar (2D) and structured (3D) silicon 44 4.1.1 Silicon (100) wafers. 44 4.1.1 Silicon Nanowires 48 4.2. Alkylation of silicon surfaces via hydrosilylation of n-alkynes 56 4.2.1. Thermal hydrosilylation on planar and nanostructured silicon substrates. 56 4.2.3. Wetting properties of alkyl modified silicon substrat	1.4.1 Strategies and Applications	10
1.4.3. Si-C bonded monolayers on oxide free silicon 15 2. Characterization methods 20 2.1. Ellipsometry 22 2.2. Contact angle Measurements 23 2.3. Infrared spectroscopy 27 2.3.1. Reflection Absorption Infrared Spectroscopy (RAIRS) 27 2.3.2. Determining surface orientation with RAIRS 30 3. Experimental 32 3.1. Chemicals and materials. 32 3.2. Substrate Preparation 35 3.3. Chemical modification of silicon substrates 36 3.4. Infrared spectroscopy measurements 39 3.5. Ellipsometric measurements 43 3.6. Contact Angle measurements 43 3.7. NMR measurements 43 3.7. NMR measurements 43 4.1 Preparation and properties of oxide-free planar (2D) and structured (3D) silicon substrates 44 4.1.1 Silicon (100) wafers. 44 4.1.2. Porous silicon 47 4.1.3. Silicon Nanowires 48 4.2. Alkylation of silicon surfaces via hydrosilylation of n-alkynes 56 4.2.1. Thermal hydrosilylation on planar and nanostructured silicon substrates 56 4.2.3. Wetting p	1.4.2. Organosilane monolayers on native, oxide-covered silicon	13
2. Characterization methods 20 2.1. Ellipsometry 22 2.2. Contact angle Measurements 23 2.3. Infrared spectroscopy 27 2.3.1. Reflection Absorption Infrared Spectroscopy (RAIRS) 27 2.3.2. Determining surface orientation with RAIRS 30 3. Experimental 32 3.1. Chemicals and materials 32 3.2. Substrate Preparation 35 3.3. Chemical modification of silicon substrates 36 3.4. Infrared spectroscopy measurements 39 3.5. Ellipsometric measurements 43 3.6. Contact Angle measurements 43 3.7. NMR measurements 43 3.8. Contact Angle measurements 44 4.1 Preparation and properties of oxide-free planar (2D) and structured (3D) silicon substrates 44 4.1 Preparation and properties of oxide-free planar (2D) and structured (3D) silicon substrates 44 4.1.1 Silicon (100) wafers 44 4.1.2. Porous silicon 47 4.1.3. Silicon Nanowires 48 4.2. Alkylation of silicon surfaces via hydrosilylation of n-alkynes 56 4.2.1. Thermal hydrosilylation on planar and nanostructured silicon substrates 6	1.4.3. Si-C bonded monolayers on oxide free silicon	15
2.1. Ellipsometry 22 2.2. Contact angle Measurements 23 2.3. Infrared spectroscopy 27 2.3.1. Reflection Absorption Infrared Spectroscopy (RAIRS) 27 2.3.2. Determining surface orientation with RAIRS 30 3. Experimental 32 3.1. Chemicals and materials 32 3.2. Substrate Preparation 35 3.3. Chemical modification of silicon substrates 36 3.4. Infrared spectroscopy measurements 39 3.5. Ellipsometric measurements 43 3.6. Contact Angle measurements 43 3.7. NMR measurements 43 4.1 Preparation and properties of oxide-free planar (2D) and structured (3D) silicon substrates 44 4.1 Preparation of silicon surfaces via hydrosilylation of n-alkynes 46 4.2. Alkylation of silicon surfaces via hydrosilylation of n-alkynes 56 4.2.1. Thermal hydrosilylation on planar and nanostructured silicon substrates 56 4.2.3. Wetting properties of alkyl modified silicon substrates 56 4.2.4. Oxidation of biare and alkylated silicon substrates 56 4.2.3. Wetting properties of alkyl modified silicon substrates 56 4.3.4. Pro	2. Characterization methods	20
2.2. Contact angle Measurements 23 2.3. Infrared spectroscopy 27 2.3.1. Reflection Absorption Infrared Spectroscopy (RAIRS) 27 2.3.2. Determining surface orientation with RAIRS 30 3. Experimental 32 3.1. Chemicals and materials 32 3.2. Substrate Preparation 35 3.3. Chemical modification of silicon substrates 36 3.4. Infrared spectroscopy measurements 39 3.5. Ellipsometric measurements 43 3.6. Contact Angle measurements 43 3.7. NMR measurements 43 3.6. Contact Angle measurements 43 3.7. NMR measurements 43 4.1 Preparation and properties of oxide-free planar (2D) and structured (3D) silicon 44 4.1.1 Silicon (100) wafers 44 4.1.1 Silicon surfaces via hydrosilylation of n-alkynes 56 4.2.1. Thermal hydrosilylation on planar and nanostructured silicon substrates 56 4.2.3. Wetting properties of alkyl modified silicon substrates 56 4.2.4. Oxidation of bare and alkylated silicon substrates 56 4.3.1. Propiolic acid mono and diesters 73 4.3.2. Reversible acid-base surface reactions	2.1. Ellipsometry	22
2.3. Infrared spectroscopy 27 2.3.1. Reflection Absorption Infrared Spectroscopy (RAIRS) 27 2.3.2. Determining surface orientation with RAIRS 30 3. Experimental 32 3.1. Chemicals and materials. 32 3.2. Substrate Preparation 35 3.3. Chemical modification of silicon substrates 36 3.4. Infrared spectroscopy measurements 39 3.5. Ellipsometric measurements 43 3.6. Contact Angle measurements 43 3.7. NMR measurements 43 3.7. NMR measurements 43 4.1 Preparation and properties of oxide-free planar (2D) and structured (3D) silicon substrates 4.1.1 Silicon (100) wafers. 45 4.1.2. Porous silicon 47 4.1.3. Silicon Nanowires 48 4.2. Alkylation of silicon surfaces via hydrosilylation of n-alkynes 56 4.2.1. Thermal hydrosilylation on planar and nanostructured silicon substrates 56 4.2.3. Wetting properties of alkyl modified silicon substrates 56 4.2.4. Oxidation of bare and alkylated silicon substrates 56 4.2.3. Wetting properties of alkyl modified silicon substrates 66 4.2.4. Oxidation	2.2. Contact angle Measurements	23
2.3.1. Reflection Absorption Infrared Spectroscopy (RAIRS) 27 2.3.2. Determining surface orientation with RAIRS 30 3. Experimental 32 3.1. Chemicals and materials 32 3.2. Substrate Preparation 35 3.3. Chemical modification of silicon substrates 36 3.4. Infrared spectroscopy measurements 39 3.5. Ellipsometric measurements 43 3.6. Contact Angle measurements 43 3.7. NMR measurements 43 4. Results and discussion 44 4.1 Preparation and properties of oxide-free planar (2D) and structured (3D) silicon substrates 4.1.1 Silicon (100) wafers. 45 4.1.2. Porous silicon 47 4.1.3. Silicon Nanowires 48 4.2. Alkylation of silicon surfaces via hydrosilylation of n-alkynes 56 4.2.1. Thermal hydrosilylation on planar and nanostructured silicon substrates 56 4.2.3. Wetting properties of alkyl modified silicon substrates 66 4.2.4. Oxidation of bare and alkylated silicon substrates 66 4.2.4. Oxidation of bare and alkylated silicon substrates 73 4.3.1. Propiolic acid mono and diesters 73	2.3. Infrared spectroscopy	27
2.3.2. Determining surface orientation with RAIRS 30 3. Experimental 32 3.1. Chemicals and materials 32 3.2. Substrate Preparation 35 3.3. Chemical modification of silicon substrates 36 3.4. Infrared spectroscopy measurements 39 3.5. Ellipsometric measurements 43 3.6. Contact Angle measurements 43 3.7. NMR measurements 43 3.7. NMR measurements 43 4.1 Preparation and properties of oxide-free planar (2D) and structured (3D) silicon substrates 4.1.1 Silicon (100) wafers. 44 4.1.2. Porous silicon 47 4.1.3. Silicon Nanowires 48 4.2. Alkylation of silicon surfaces via hydrosilylation of n-alkynes 56 4.2.1. Thermal hydrosilylation on planar and nanostructured silicon substrates 56 4.2.3. Wetting properties of alkyl modified silicon surfaces 69 4.3. Adsorption of activated alkynes 73 4.3.1. Propiolic acid mono and diesters 73 4.3.2. Reversible acid-base surface reactions of adsorbed propiolic acid 76 4.4. Surface functionalization via click chemistry 80 4.4.1. Copper-tree click r	2.3.1. Reflection Absorption Infrared Spectroscopy (RAIRS)	27
3. Experimental 32 3.1. Chemicals and materials 32 3.2. Substrate Preparation 35 3.3. Chemical modification of silicon substrates 36 3.4. Infrared spectroscopy measurements 39 3.5. Ellipsometric measurements 43 3.6. Contact Angle measurements 43 3.7. NMR measurements 43 3.7. NMR measurements 43 4. Results and discussion 44 4.1 Preparation and properties of oxide-free planar (2D) and structured (3D) silicon substrates substrates 45 4.1.2. Porous silicon 47 4.1.3. Silicon Nanowires 48 4.2. Alkylation of silicon surfaces via hydrosilylation of n-alkynes 56 4.2.1. Thermal hydrosilylation on planar and nanostructured silicon substrates 56 4.2.2. Surface orientation of alkyne monolayers on Si (100) wafers 58 4.2.3 Wetting properties of alkyl modified silicon substrates 66 4.3. Adsorption of activated alkynes 73 4.3.1. Propiolic acid mono and diesters 73 4.3.2. Reversible acid-base surface reactions of adsorbed propiolic acid 76 4.4. Surface functionalization via click chemistry	2.3.2. Determining surface orientation with RAIRS	30
3.1. Chemicals and materials 32 3.2. Substrate Preparation 35 3.3. Chemical modification of silicon substrates 36 3.4. Infrared spectroscopy measurements 39 3.5. Ellipsometric measurements 43 3.6. Contact Angle measurements 43 3.7. NMR measurements 43 3.7. NMR measurements 43 3.7. NMR measurements 43 4.1 Preparation and properties of oxide-free planar (2D) and structured (3D) silicon 44 4.1.1 Silicon (100) wafers 45 4.1.2. Porous silicon 47 4.1.3. Silicon Nanowires 48 4.2. Alkylation of silicon surfaces via hydrosilylation of n-alkynes 56 4.2.1. Thermal hydrosilylation on planar and nanostructured silicon substrates 56 4.2.3. Wetting properties of alkyl modified silicon substrates 66 4.2.4. Oxidation of bare and alkylated silicon surfaces 69 4.3. Alsorption of activated alkynes 73 4.3.1. Propiolic acid mono and diesters 73 4.3.2. Reversible acid-base surface reactions of adsorbed propiolic acid. 76 4.4. Surface functionalization via click chemistry 80 4.4.1. Copper cataly	3. Experimental	32
3.2. Substrate Preparation 35 3.3. Chemical modification of silicon substrates 36 3.4. Infrared spectroscopy measurements 39 3.5. Ellipsometric measurements 43 3.6. Contact Angle measurements 43 3.7. NMR measurements 43 4. Results and discussion 44 4.1 Preparation and properties of oxide-free planar (2D) and structured (3D) silicon 44 4.1.1 Silicon (100) wafers 45 4.1.2. Porous silicon 47 4.1.3. Silicon Nanowires 48 4.2. Alkylation of silicon surfaces via hydrosilylation of n-alkynes 56 4.2.1. Thermal hydrosilylation on planar and nanostructured silicon substrates 56 4.2.2. Surface orientation of alkyne monolayers on Si (100) wafers 58 4.2.3 Wetting properties of alkyl modified silicon substrates 66 4.2.4. Oxidation of bare and alkylated silicon surfaces 69 4.3. Adsorption of activated alkynes 73 4.3.2. Reversible acid-base surface reactions of adsorbed propiolic acid. 76 4.4. Surface functionalization via click chemistry 80 4.4.1. Copper catalysed Huisgen cycloadditions. 80 4.4.2. Copper-free click reactions	3.1. Chemicals and materials	32
3.3. Chemical modification of silicon substrates 36 3.4. Infrared spectroscopy measurements 39 3.5. Ellipsometric measurements 43 3.6. Contact Angle measurements 43 3.7. NMR measurements 43 4.7. Results and discussion 44 4.1 Preparation and properties of oxide-free planar (2D) and structured (3D) silicon 44 4.1.1 Preparation and properties of oxide-free planar (2D) and structured (3D) silicon 44 4.1.1 Silicon (100) wafers 44 4.1.2. Porous silicon 47 4.1.3. Silicon Nanowires 48 4.2. Alkylation of silicon surfaces via hydrosilylation of n-alkynes 56 4.2.1. Thermal hydrosilylation on planar and nanostructured silicon substrates 56 4.2.2. Surface orientation of alkyne monolayers on Si (100) wafers 58 4.2.3 Wetting properties of alkyl modified silicon substrates 66 4.2.4. Oxidation of bare and alkylated silicon substrates 69 4.3. Alsorption of activated alkynes 73 4.3.1. Propiolic acid mono and diesters 73 4.3.2. Reversible acid-base surface reactions of adsorbed propiolic acid 76 4.4. Surface functionalization via click chemistry 80	3.2. Substrate Preparation	35
3.4. Infrared spectroscopy measurements 39 3.5. Ellipsometric measurements 43 3.6. Contact Angle measurements 43 3.7. NMR measurements 43 4. Results and discussion 44 4.1 Preparation and properties of oxide-free planar (2D) and structured (3D) silicon substrates 44 4.1.1 Silicon (100) wafers. 45 4.1.2. Porous silicon 47 4.1.3. Silicon Nanowires 48 4.2. Alkylation of silicon surfaces via hydrosilylation of n-alkynes 56 4.2.1. Thermal hydrosilylation on planar and nanostructured silicon substrates 56 4.2.3. Wetting properties of alkyle monolayers on Si (100) wafers 58 4.2.3. Wetting properties of alkyled silicon surfaces 69 4.3. Adsorption of activated alkynes 73 4.3.1. Propiolic acid mono and diesters 73 4.3.2. Reversible acid-base surface reactions of adsorbed propiolic acid. 76 4.4. Surface functionalization via click chemistry 80 4.4.1. Copper catalysed Huisgen cycloadditions. 80 4.4.2. Copper-free click reactions 82 5. Conclusion and Perspectives 92 6. References 92 <td>3.3. Chemical modification of silicon substrates</td> <td> 36</td>	3.3. Chemical modification of silicon substrates	36
3.5. Ellipsometric measurements 43 3.6. Contact Angle measurements 43 3.7. NMR measurements 43 4.1 Results and discussion 44 4.1 Preparation and properties of oxide-free planar (2D) and structured (3D) silicon 44 4.1.1 Silicon (100) wafers. 44 4.1.1 Silicon (100) wafers. 45 4.1.2. Porous silicon 47 4.1.3. Silicon Nanowires 48 4.2. Alkylation of silicon surfaces via hydrosilylation of n-alkynes. 56 4.2.1. Thermal hydrosilylation on planar and nanostructured silicon substrates. 56 4.2.3. Wetting properties of alkyle monolayers on Si (100) wafers 58 4.2.3. Wetting properties of alkyl modified silicon surfaces 69 4.3.1. Propiolic acid mono and diesters 73 4.3.2. Reversible acid-base surface reactions of adsorbed propiolic acid. 76 4.4. Surface functionalization via click chemistry. 80 4.4.1. Copper catalysed Huisgen cycloadditions. 80 4.4.2. Copper-free click reactions 82 5. Conclusion and Perspectives 92 6. References 92	3.4. Infrared spectroscopy measurements	39
3.6. Contact Angle measurements. 43 3.7. NMR measurements. 43 4. Results and discussion. 44 4.1 Preparation and properties of oxide-free planar (2D) and structured (3D) silicon substrates. 44 4.1.1 Silicon (100) wafers. 44 4.1.2. Porous silicon 47 4.1.3. Silicon Nanowires 48 4.2. Alkylation of silicon surfaces via hydrosilylation of n-alkynes 56 4.2.1. Thermal hydrosilylation on planar and nanostructured silicon substrates. 56 4.2.2. Surface orientation of alkyne monolayers on Si (100) wafers 58 4.2.3 Wetting properties of alkyl modified silicon substrates. 66 4.2.4. Oxidation of bare and alkylated silicon surfaces 69 4.3.1. Propiolic acid mono and diesters 73 4.3.2. Reversible acid-base surface reactions of adsorbed propiolic acid. 76 4.4. Surface functionalization via click chemistry. 80 4.4.1. Copper catalysed Huisgen cycloadditions. 80 4.4.2 Copper-free click reactions 82 5. Conclusion and Perspectives. 92 6. References 95	3.5. Ellipsometric measurements	43
3.7. NMR measurements43 4. Results and discussion 444.1 Preparation and properties of oxide-free planar (2D) and structured (3D) siliconsubstrates444.1.1 Silicon (100) wafers454.1.2. Porous silicon474.1.3. Silicon Nanowires484.2. Alkylation of silicon surfaces via hydrosilylation of n-alkynes564.2.1. Thermal hydrosilylation on planar and nanostructured silicon substrates564.2.2. Surface orientation of alkyne monolayers on Si (100) wafers584.2.3 Wetting properties of alkyl modified silicon substrates664.2.4. Oxidation of bare and alkylated silicon surfaces694.3. Adsorption of activated alkynes734.3.1. Propiolic acid mono and diesters734.3.2. Reversible acid-base surface reactions of adsorbed propiolic acid.764.4. Surface functionalization via click chemistry804.4.1. Copper catalysed Huisgen cycloadditions825. Conclusion and Perspectives926. References95	3.6. Contact Angle measurements	43
4. Results and discussion444.1 Preparation and properties of oxide-free planar (2D) and structured (3D) siliconsubstrates444.1.1 Silicon (100) wafers454.1.2. Porous silicon474.1.3. Silicon Nanowires484.2. Alkylation of silicon surfaces via hydrosilylation of n-alkynes564.2.1. Thermal hydrosilylation on planar and nanostructured silicon substrates564.2.2. Surface orientation of alkyne monolayers on Si (100) wafers584.2.3 Wetting properties of alkyl modified silicon substrates664.2.4. Oxidation of bare and alkylated silicon surfaces694.3. Adsorption of activated alkynes734.3.1. Propiolic acid mono and diesters734.3.2. Reversible acid-base surface reactions of adsorbed propiolic acid.764.4. Surface functionalization via click chemistry804.4.1. Copper catalysed Huisgen cycloadditions.804.4.2 Copper-free click reactions825. Conclusion and Perspectives926. References95	3.7. NMR measurements	43
4.1 Preparation and properties of oxide-free planar (2D) and structured (3D) siliconsubstrates.444.1.1 Silicon (100) wafers.454.1.2. Porous silicon474.1.3. Silicon Nanowires484.2. Alkylation of silicon surfaces via hydrosilylation of n-alkynes.564.2.1. Thermal hydrosilylation on planar and nanostructured silicon substrates.564.2.2. Surface orientation of alkyne monolayers on Si (100) wafers584.2.3 Wetting properties of alkyl modified silicon substrates.664.2.4. Oxidation of bare and alkylated silicon surfaces694.3. Adsorption of activated alkynes734.3.1. Propiolic acid mono and diesters734.3.2. Reversible acid-base surface reactions of adsorbed propiolic acid.764.4. Surface functionalization via click chemistry804.4.1. Copper catalysed Huisgen cycloadditions.825. Conclusion and Perspectives926. References95	4. Results and discussion	44
substrates.444.1.1 Silicon (100) wafers.454.1.2. Porous silicon	4.1 Preparation and properties of oxide-free planar (2D) and structured (3D) silicon	
4.1.1 Silicon (100) wafers.454.1.2. Porous silicon474.1.3. Silicon Nanowires484.2. Alkylation of silicon surfaces via hydrosilylation of n-alkynes.564.2.1. Thermal hydrosilylation on planar and nanostructured silicon substrates.564.2.2. Surface orientation of alkyne monolayers on Si (100) wafers584.2.3 Wetting properties of alkyl modified silicon substrates664.2.4. Oxidation of bare and alkylated silicon surfaces694.3. Adsorption of activated alkynes734.3.1. Propiolic acid mono and diesters734.3.2. Reversible acid-base surface reactions of adsorbed propiolic acid764.4. Surface functionalization via click chemistry804.4.1. Copper catalysed Huisgen cycloadditions825. Conclusion and Perspectives926. References95	substrates.	44
4.1.2. Porous silicon474.1.3. Silicon Nanowires484.2. Alkylation of silicon surfaces via hydrosilylation of n-alkynes564.2.1. Thermal hydrosilylation on planar and nanostructured silicon substrates564.2.2. Surface orientation of alkyne monolayers on Si (100) wafers584.2.3 Wetting properties of alkyl modified silicon substrates664.2.4. Oxidation of bare and alkylated silicon surfaces694.3. Adsorption of activated alkynes734.3.1. Propiolic acid mono and diesters734.3.2. Reversible acid-base surface reactions of adsorbed propiolic acid764.4.1. Copper catalysed Huisgen cycloadditions804.4.2 Copper-free click reactions825. Conclusion and Perspectives926. References95	4.1.1 Silicon (100) wafers.	45
4.1.3. Silicon Nanowires484.2. Alkylation of silicon surfaces via hydrosilylation of n-alkynes564.2.1. Thermal hydrosilylation on planar and nanostructured silicon substrates564.2.2. Surface orientation of alkyne monolayers on Si (100) wafers584.2.3 Wetting properties of alkyl modified silicon substrates664.2.4. Oxidation of bare and alkylated silicon surfaces694.3. Adsorption of activated alkynes734.3.1. Propiolic acid mono and diesters734.3.2. Reversible acid-base surface reactions of adsorbed propiolic acid764.4.1. Copper catalysed Huisgen cycloadditions804.4.2 Copper-free click reactions825. Conclusion and Perspectives926. References95	4.1.2. Porous silicon	47
4.2. Alkylation of silicon surfaces via hydrosilylation of n-alkynes.564.2.1. Thermal hydrosilylation on planar and nanostructured silicon substrates.564.2.2. Surface orientation of alkyne monolayers on Si (100) wafers584.2.3 Wetting properties of alkyl modified silicon substrates664.2.4. Oxidation of bare and alkylated silicon surfaces694.3. Adsorption of activated alkynes734.3.1. Propiolic acid mono and diesters734.3.2. Reversible acid-base surface reactions of adsorbed propiolic acid.764.4. Surface functionalization via click chemistry804.4.1. Copper catalysed Huisgen cycloadditions.804.4.2 Copper-free click reactions825. Conclusion and Perspectives926. References95	4.1.3. Silicon Nanowires	48
4.2.1. Thermal hydrosilylation on planar and nanostructured silicon substrates.564.2.2. Surface orientation of alkyne monolayers on Si (100) wafers584.2.3 Wetting properties of alkyl modified silicon substrates664.2.4. Oxidation of bare and alkylated silicon surfaces694.3. Adsorption of activated alkynes734.3.1. Propiolic acid mono and diesters734.3.2. Reversible acid-base surface reactions of adsorbed propiolic acid.764.4. Surface functionalization via click chemistry804.4.1. Copper catalysed Huisgen cycloadditions.804.4.2 Copper-free click reactions825. Conclusion and Perspectives926. References95	4.2. Alkylation of silicon surfaces via hydrosilylation of n-alkynes	56
4.2.2. Surface orientation of alkyne monolayers on Si (100) wafers584.2.3 Wetting properties of alkyl modified silicon substrates664.2.4. Oxidation of bare and alkylated silicon surfaces694.3. Adsorption of activated alkynes734.3.1. Propiolic acid mono and diesters734.3.2. Reversible acid-base surface reactions of adsorbed propiolic acid.764.4. Surface functionalization via click chemistry804.4.1. Copper catalysed Huisgen cycloadditions804.4.2 Copper-free click reactions825. Conclusion and Perspectives926. References95	4.2.1. Thermal hydrosilylation on planar and nanostructured silicon substrates	56
4.2.3 Wetting properties of alkyl modified silicon substrates664.2.4. Oxidation of bare and alkylated silicon surfaces694.3. Adsorption of activated alkynes734.3.1. Propiolic acid mono and diesters734.3.2. Reversible acid-base surface reactions of adsorbed propiolic acid764.4. Surface functionalization via click chemistry804.4.1. Copper catalysed Huisgen cycloadditions804.4.2 Copper-free click reactions825. Conclusion and Perspectives926. References95	4.2.2. Surface orientation of alkyne monolayers on Si (100) wafers	58
4.2.4. Oxidation of bare and alkylated silicon surfaces694.3. Adsorption of activated alkynes734.3.1. Propiolic acid mono and diesters734.3.2. Reversible acid-base surface reactions of adsorbed propiolic acid764.4. Surface functionalization via click chemistry804.4.1. Copper catalysed Huisgen cycloadditions804.4.2 Copper-free click reactions825. Conclusion and Perspectives926. References95	4.2.3 Wetting properties of alkyl modified silicon substrates	66
4.3. Adsorption of activated alkynes734.3.1. Propiolic acid mono and diesters734.3.2. Reversible acid-base surface reactions of adsorbed propiolic acid.764.4. Surface functionalization via click chemistry804.4.1. Copper catalysed Huisgen cycloadditions.804.4.2 Copper-free click reactions825. Conclusion and Perspectives926. References95	4.2.4. Oxidation of bare and alkylated silicon surfaces	69
4.3.1. Propiolic acid mono and diesters 73 4.3.2. Reversible acid-base surface reactions of adsorbed propiolic acid. 76 4.4. Surface functionalization via click chemistry 80 4.4.1. Copper catalysed Huisgen cycloadditions. 80 4.4.2 Copper-free click reactions 82 5. Conclusion and Perspectives 92 6. References 95	4.3. Adsorption of activated alkynes	73
4.3.2. Reversible acid-base surface reactions of adsorbed propiolic acid. 76 4.4. Surface functionalization via click chemistry 80 4.4.1. Copper catalysed Huisgen cycloadditions. 80 4.4.2 Copper-free click reactions 82 5. Conclusion and Perspectives 92 6. References 95	4.3.1. Propiolic acid mono and diesters	73
4.4. Surface functionalization via click chemistry 80 4.4.1. Copper catalysed Huisgen cycloadditions 80 4.4.2 Copper-free click reactions 82 5. Conclusion and Perspectives 92 6. References 95	4.3.2. Reversible acid-base surface reactions of adsorbed propiolic acid	76
4.4.1. Copper catalysed Huisgen cycloadditions	4.4. Surface functionalization via click chemistry	80
4.4.2 Copper-free click reactions	4.4.1. Copper catalysed Huisgen cycloadditions	80
5. Conclusion and Perspectives	4.4.2 Copper-free click reactions	82
6. References	5. Conclusion and Perspectives	92
	6. References	95

1. Introduction

1.1. Silicon Wafers

Semiconductors, materials which have electric conductances between metals and insulators, are the key components of integrated circuits in any electronic equipment today with silicon as the by far most common material employed since the beginning of the semiconductor revolution decades ago. Silicon is a cheap and high quality semiconductor, which, as the most abundant element on earth, is easily accessible and can be refined to purities exceeding 9.9 (99.9999999%), thereby prevailing over more efficient semiconductor materials like germanium with higher conductivities. Three important parameters that characterize silicon wafers are the purity, the doping and the crystal orientation. The manufacturing of silicon wafers is a slow process involving high purity, polycrystalline Si as the raw product which is melted in a crucible at 1600°C. A seed crystal is immersed into the molten silicon and rotated, resulting in the growth of a pure silicon cylinder called an ingot. Cutting the silicon crystal into thin discs called wafers results in silicon surfaces aligned in one of several directions known as crystal orientations. The most common orientations are Si(100), Si(111) and Si(110). Orientation is important since many of a single crystal's structural and electronic properties are highly anisotropic and wafer cleavage typically occurs only in a few well-defined directions. Si(100) is the material that is currently used in the majority of semiconductor devices largely because of a fortunate matching of the interatomic spacing of silicon atoms with the lattice constant of silicon dioxide¹

In order to influence the conductance of the silicon crystal, these are often impurified with very small amounts of phosphorous or boron that are generally added to the molten raw silicon during wafer fabrication, such impurification being called doping. Phosphorous atoms are integrated into the silicon-crystal-structure but they have one extra valence electron making the crystal slightly negative (n-silicon). Boron, on the contrary, has one less valence electron hence inducing an electron hole into the the silicon crystal, making it slightly positive (p-silicon). Controlled doping is the basis of modern semiconductor technology.

Oxide etch of crystalline silicon

Bare silicon surfaces are highly reactive and rapidly form a native oxide layer with a thickness of several Ångström when exposed to the atmosphere. To remove this native oxide, the silicon is exposed to a dilute HF-solution which dissolves the native oxide into hexafluorosilicic acid. Based on the fact that Si and F form one of the strongest bonds known, it would seem quite obvious that the silicon surface after being treated and etched with HF is passivated with F. that is not the case, however. In fact, not even traces of F can be detected on the surface, neither with FTIR nor with XPS. Instead it is fully covered with hydrogen. The reason for the lack of Si-F bonds is that although it is a strong bond, it is also highly polar, causing strain to the silicon lattice and polarizing the adjacent Si-Si bonds which makes them sensitive to nucleophilic attacks.

In comparison, the Si-H bond is an unpolar bond, with its electrons almost evenly shared between silicon and hydrogen. Such bonds are similar to the Si-Si bonds in the bulk and relieve strain to the lattice. Hence, etching silicon oxide with dilute HF results in an almost perfect H-terminated Si surface. Si(111) is terminated with Si-H monohydrides (Fig 1.1) and forms a perfectly flat crystal surface. H-terminated Si(100) surfaces, however, form a mixture of mono, di- and tri-hydrides which due to unfavourable steric interactions inhibit the formation of a perfectly flat surface and a roughness of approximately 3 Å remains.



Figur 1.1. Etching of Si(100) and Si(111) in fluoride solutions (Scheme taken from Ref.1)

1.2. Porous Silicon

Porous silicon is structured bulk silicon with nanoporous holes and of typically 1-100 nm diameter and surface to volume ratios of several 100 m²/cm³, which change the properties of the material dramatically. It was accidently discovered in the mid 1950s by Ingeborg and Arthur Uhlir at Bell Laboratories in their attempt to electropolish silicon surfaces, using aqueous solutions of HF. They noticed that under certain conditions the polishing resulted in an unwanted uneven and sometimes coloured surface instead of the expected smooth, polished surface. They did not explore this discovery further and it was pretty much ignored until the late 1980s, when the porous nature, high surface area and the true surface composition (siliconhydride) of this material was revealed and raised a moderate interest^{2,3,4}. A paper in 1990 by Chanman et al, describing room temperature visible photo luminescence of porous silicon probably caused by quantum confinement, further drew the world wide attention to this material, extensively raising the number of studies from about 200 papers reported until 1990 to about 1500 papers 6 years later⁴. It has now opened new fields of research and a current scifinder-search on porous silicon yields over 12000 hits. The discovery of the quantum effects of porous silicon made it an interesting material for several reasons 1) The contrast to planar silicon that is spectacularly inefficient at emitting light even at cryogenic condition. 2) Porous silicon can be easily and cheaply prepared in a standard chemistry labl in large quantities and time scales of e few minutes. 3) Since Si is technologically still the most important material that dominates the microelectronic industry. light-emitting Si devices may eventually result in a new generation of Si chips and extend the functionality of Si technology from microelectronics into optoelectronics⁴. Apart from photoluminescence, porous silicon has a number of other interesting properties for practical applications:

It has a very large surface area to volume ratio (hundreds of m² per cm³), making it a useful high surface area substrate for spectroscopic studies and for sensor devices². Porous silicon has an increased band gap compared to planar silicon⁵, that and the larger surface area make it interesting in photovoltaic applications⁶. Porous silicon seems to be biologically compatible and has been used for drug delivery^{7,8} and as a substrate for in-vivo sensors^{9,10}

Silicon Porosification

Porous silicon is formed by anisotropic etching of silicon wafers in HF solutions. As already mentioned, bare silicon surfaces are essentially inert towards HF solution with an etching rate in concentrated HF as slow as 0.3 Å/min. Hence, the first step in silicon etching is to activate the surface, which is achieved by creating an electron hole in the valence band by

exciting an electron from the valence band to the conduction band. This is the most essential part of silicon etching that will increase the etching rate and allow control of the etching. The holes in the valence band can be created by applying a galvanic bias voltage, by photon absorption or by adding an oxidant. The holes are transported to the surface of the bulk silicon, where they weaken the bonds nearby and hence making these positions more sensitive¹¹.

A mechanism proposed by Gerischer et al and subsequently corrected by Kolanski¹¹ and coworkers is shown in Fig 1.2. The first and crucial step is always the creation of an electron hole, which is transported to the surface. At the surface it weakens the Si-H bond and results in its heterolytic cleavage, whereby a proton is released and one electron is transported to the conduction band, leaving a Si radical behind. This radical reacts with a fluoride ione under formation of a Si-F bond and transfer of one electron to the silicon valence band. Altogether, in this first 4 step, a Si-H bond is exchanged to a Si-F bond, a proton is abstracted and an electron is transferred to the conduction band. Alternatively, the reaction may proceed through a S_N2 mechanism with the same end result.

Once the H-passivation is broken by F-substituion, the surface is sensitive to nucleophilic attack also without additional electron holes. This is because the Si-F bond is highly polar causing strain to the silicon lattice and polarizing the silicon backbone as already described in chapter 1.1. The next step is therefore a nucleophilic attack by a fluoride ion breaking a Si-Si bond followed by a hydrogen transfer to the adjacent Si. Subsequently, two different reaction paths are possible: Path a repeats the last step resulting in a cleavage of SiHF₃ which reacts with HF in solution to form SiF₆²⁻ and H₂(g). In path b, a second proton is abstracted and a second electron is donated to the conduction band forming a silicon radical. A fluoride attacks the Si, donating an additional electron to the conduction band. A nucleophilic attack of an additional fluoride yields SiF₄ as the cleavage product, which in solution with excess HF forms again SiF₆²⁻.

The overall etching reaction following path a is described as

Si + h^+ + 6HF \longrightarrow H_2SiF_6 + 2H+ + H_2 + e^-_{CB}

This path is synonymous for a process called current doubling, as every electron hole induced in the valence band yields 2 electrons in the conduction band, resulting in photocurrent quantum yield of two.

The path b is synonymous for current quadrupling, as every induced hole in the valence band yields 4 electrons in the conduction band.

Si + h⁺ + 6HF \longrightarrow H₂SiF₆ + 4H⁺ + 3e⁻_{CB}



Figure 1. 2. Proposed mechanisms for anisotropic etching of silicon¹¹

Other mechanisms has been proposed¹², however, an electron hole at the surface, that weakens the Si-H bond and makes it sensitive to nucleophilic attack is the essential part of silicon etching. Surface electron holes are also a prerequisite for anisotropic etching that does not lead to the complete dissolution of silicon but to the formation of pores. The transport of holes to the surface is controlled by quantum confinement effects which, once the structures reach nanoscale dimensions, passivate small structures and direct holes to the bottom of pores rather than to pore walls.

1.3. Silicon Nanowires

Silicon nanowires (SiNW) are considered as one-dimensional semiconducting structures and have shown novel electronic, optical, mechanical, thermal, and chemical properties. They are expected to play a key role in applications such as solar cells¹³⁻¹⁶, sensors¹⁷⁻¹⁹, lithium batteries²⁰, and catalysts with regard to their surface-determined properties. The high surface to volume ratios of silicon nanowires make their material characteristics to be dominated by their surface properties rather than their bulk structure, hence they differ from bulk silicon in many ways and form unique materials. Generally, changing the diameter of the nanowires will change their properties. Nanowires with a diameter of less than 44 nm will oxidize essentially slower in ambient atmosphere compared to bulk silicon due to compressive stress normal to Si/SiO₂ interface, which arises from the greater volume of SiO₂ compared to Si²¹. Also, the electric and thermal conductance is correlated to the nanowire diameter. Hence, control of the nanowire diameter allows tuning of some important properties. Silicon nanowires are also a very promising material in solar cell applications due to its very efficient light absorption and negligible reflection. SiNW based solar cells have the potential to increase the conversion efficiency substantially compared to bulk silicon. It is also expected to allow cheap silicon with a high level of impurities and a large degree of defects to be used in solar cells, hence reducing the costs substantially. Such cheap low quality silicon results in low minority diffusion lengths, which is the average distance a charge carrier can move from its point of generation until it recombines. Hence, the energy conversion of such low-minority conversion lengths material is on planar substrates limited by the minority carrier diffusion, independent of the layer thickness. An increase in the thickness will produce more light absorption but it will not result in an increase in the device efficiency due to charge recombination. Nanowires are superior, in comparison, because they are long in one dimension allowing maximal absorption and thin in another dimension, thereby allowing effective carrier collection²².

Silicon Nanowire Fabrication

Several different synthetic routes for the preparation of silicon nanowires, based on either gas-phase or condensed-phase techniques, are known today. Nanowire formation can generally be divided into bottom-up techniques and top-down approaches, where the bottom-up approach involves growing Si-NWs from molecular precursor whereas in the top-down approach bulk silicon is the starting material.

The bottom-up approach

The by far most frequently applied approach to form silicon nanowires is via the vapourliquid-solid (VLS) method by chemical vapour deposition (CVD). Briefly, in this process Si-NWs grow on a silicon substrate in the presence of gaseous silicon precursors such as tetrahydrosilane (SiH₄) and a metal catalyst that is immobilized on the surface and is capable of forming a low temperature eutectic phase with silicon. A thin metal film is first immobilized onto the surface and as the surface is subsequently heated above the metal-silicon eutectic temperature, alloy droplets are formed on the wafer. In the presence of the precursor molecules, silicon will diffuse into this drop, which eventually will be supersaturated leading to the precipitation of Si on the wafer-alloy interface. The alloy drop will remain above the precipitated Si allowing further anisotropic Si NW growth^{23,24}.



Figure 1. 3. Schematic figure illustrating the nanowire growth vapour-liquid-solid (VLS) method by chemical vapour deposition (CVD)

Although nanowire growth can be catalyzed by many metals, gold is the most common material used for several reasons: it is 1) nontoxic, 2) chemically inert, and easily available, 3) it has an eutectic point in the Au/Si binary system at a low temperature (340°C) and high Si solubility, 4) it has a low vapour pressure at elevated temperatures, and 5) the Au–Si liquid alloy has a high-enough surface tension to form droplets on the surface. However, incompatibility with industrial electronic production standards is a major drawback of Au, hence other metals should be further explored for this purpose. Until now, Ag has been the most promising alternative metal catalyst. The VLS technique is widely used and allows nanowires with a large range of lengths and diameters to be fabricated. By incorporating impurities it also allows controlled doping^{23,24}.

The top-down approach

In the top-down approach, high quality bulk silicon is the starting material and through techniques such as photolithography²⁵, wet and dry etching, e-beam lithography and micromachining are nanowires formed. In contrast to bottom-up methods, which usually require complex equipment, high temperatures, high vacuum and hazardous silicon precursors all of which drastically increase the cost of the processes, top down approaches are generally simpler, more cost effective and suitable for large scale production²⁶.

One rather new top-down approach that is highly promising in this respect is metal assisted electroless etching in HF solutions. It enables the fabrication of vertically aligned SiNWs at low cost in large scale²⁷. Recent improvements in the etching techniques allow the production of well-defined nanowires of high quality, etched vertically as well as diagonally dependant on the substrate's orientation (Si(100) or Si (111)). The SiNWs formed by this method will also render the properties of the silicon substrate such as the doping. SiNW prepared with the VLS technique, on the other hand, need to be doped separately by incorporating impurities during the NW growth.

Briefly, this process starts with the deposition of Ag nano-particles on a silicon wafer surface via galvanic displacement in a HF/Ag solution as shown in fig 1.4. Under proper conditions with HF and AgNO₃ kept in a narrow concentration range (4.5 M and 0.1-0.5 M respectively), the reduced Ag-particles will form a dendrimeric structure at the silicon surface. These immobilized particles will catalyse the subsequent etching in an etchant solution containing HF and H₂O₂. This allows silicon to rapidly dissolve underneath the Ag particles, forming an uniform array of silicon pillars²⁸.



Figure 1.4. Electroless etching of silicon nanowire

There are different theories on how the silver particle participates in the reaction and catalyses the etching. Zhu et al²⁹ proposed that the metal catalyst facilitates the silicon etching but will not participate in the reaction. Their hypothesis is that the etching process is the combined result of the formation of local electrochemical cells at the silicon surface, originated by the adsorption of metal NPs, and of the presence of hydrogen peroxide. They proposed that H_2O_2 is reduced to water at the adsorbed metal NPs and that the availability of an oxidizing agent with a redox potential located at an energy lower than the valence band edge of Si ($E_0 H_2O_2/H_2O = 1.763$ VSHE, corresponding to -6.263 eV, to be compared with the ionization energy of Si, -5.17 eV) makes it energetically favourable for electrons from silicon to participate in this reduction process. Hence, the metal particle stays intact whereas electron holes occur on the silicon surface. Silicon etching then proceeds as described in section 1.2.

In contrast, Zhang et. al^{28} proposed that the Ag NP is partly oxidized and partially dissolved in solution to form Ag⁺ ions immediately after being exposed to the HF/H₂O₂ solution. The dissolved Ag⁺ ions then quickly react with the Si at the interfaces between the wafer and the AgNPs, oxidizing and dissolving Si. The result is that the Ag NP will drill into the silicon surfaces eventually forming a SiNW array.

The reactions proposed according to this mechanism are

Si + 4Ag⁺ + 6F⁻ \rightarrow 4Ag + SiF₆²⁻ 2Ag + H₂O₂ + 2H⁺ \rightarrow 2Ag⁺ + 2H₂O

Yielding the overall reaction

 $Si + 6HF^- + 2H_2O_2 \rightarrow H_2SiF_6 + 4H_2O$

As the etching continuous, some Ag⁺ ions formed by this reaction may diffuse to the solution, hence, reducing the size of the AgNPs. This would explain the cone shaped forms sometimes seen on etched silicon nanowires, where more silicon has been etched at the top of the wire compared to on the bottom.

1.4. Functional Silicon Surfaces based on Self Assembled Monolayers

1.4.1 Strategies and Applications

Silicon has a number of interesting properties and although it is for decades now the standard semiconductor in electronic devices there are still enormous untapped potentials for applications in diverse fields such as photoemission, energy transfer, sensors etc.

One field that has gained intense attention over the last 20 years is surface functionalization with organic molecules. A molecular thin film on the surface can change the properties of the substrate dramatically and thanks to the compatibility of silicon with conventional electronics and the ease by which it can be structured, silicon is an ideal substrate for molecular nano devices and allows it to be employed in such different applications such as sensing devices^{19,30–32} catalysts³³, electronic devices and biomimetic surfaces^{34,35}. Electric properties of H-terminated, oxidized and methyl terminated Si nanowires were compared by Haick and co-workers³⁷ and they found a 4- and 7-fold increase in conductance on H-terminated respectively methyl terminated surfaces. Hence it is clear that the electronic properties of the substrate can be substantially influenced by surface functionalization. Recent research explores this further and has aimed at controlled tuning of the electronic properties such as the conductivity. Controlling these properties is fundamental in semiconductor devices like field-effect- transistors (FET) and is now largely achieved by gating and impurity doping. However, as semiconductor devices shrink to nanoscale dimensions such as single nanowires, routine methods may fail to achieve homogenous doping. Hence, great effort has been spent lately, aiming to develop alternative doping strategies^{38,39,40,41,42}. One approach is to immobilize a thin organic monolayer film carrying electron deficient or electron rich groups onto the surface. Charge transfer can then occur between the silicon surface and the

grafted molecules, influencing the electronic properties³⁸. The large surface-to-volume ratio of porous silicon provides high-efficiency surface modification and functionalized silicon nanowires can among others be employed to control the conductance in silicon nanowire transistors.



Figur 1. 5. Some applications of self-assembled monolayers in nanotechnology (Scheme taken from Ref36)

Sensors devices is another hot topic which has been employed for various applications. Lately a nanowire FET-sensor has been developed that allows label free detection of DNA⁴³ and volatile organic compounds⁴⁴. One other topic extensively studied is energy conversion and among others photovoltaic applications⁴⁵ and the hydrogen evolution reaction (HER) where water is spitted forming hydrogen gas⁴⁶. Most semiconductor surfaces, including silicon, are poor catalysts for this reaction. Semiconductor water-splitting devices, then, generally require a chemically distinct catalyst in order to store energy as molecular hydrogen. Platinum has often been used in the past for this purpose, since it catalyzes the HER very efficiently. Masuda et al³³ demonstrated that if Pt complexes are placed at controlled positions at silicon surfaces they act as confined molecular electrocatalysts for hydrogen evolution at a semiconductor electrode surface without being converted into metal clusters or particles.

To enable such applications surface films with well-defined packing and density of specific molecules as well as full control of the formation of these films are required. A molecular

nano device demands a high level of control over the reactivity and structure of the modified surfaces as well as a very high quality of the molecular film attached to the surface. Reliable protocols to prepare functional surfaces that for example, contain components to couple a further functionality or components that can interact with the environment are required. Molecular films fulfilling these demands can be prepared using the Langmuir-Blodgett methodology, which is a well established and sophisticated technique to form laterally structured monolayers⁴⁷ These films are formed when amphiphilic, surfactant-like molecules are placed at the air-water interface. The hydrophilic head groups are attracted to the water and the hydrophobic tail groups organize and pack themselves to form an ordered monolayer.

Another common modification procedure is to use self-assembled monolayers which can be described as a chemisorbed layer of organic molecules that under certain conditions spontaneously organize to form ordered, well defined adsorbate layers. The substrate is typically immersed into a solution of amphiphilic precursor molecules, containing a head group with a high affinity to the substrate and a hydrophobic tail group that through van der Waals interactions adopt a uniform, densely packed surface orientation with uniaxial symmetry around the surface normal. Due to their covalent bonding to the substrate, these layers are generally more stable than Langmuir-Blodgett films. Self-assembled monolayers were discovered through the adsorption of alkylsulfides on gold substrates almost 30 years ago and have been a hot topic over the last 10-15 years with a steeply increasing number of publications and applications in the a wide variety of fields³⁶. SAM modification protocols are, in addition to silicon, also available for other substrates, such as gold³⁶, silver⁴⁸, platinum⁴⁹, glass⁵⁰, and various metal- and metalloid oxides⁵¹. The monolayers can be attached to the substrate by covalent, ionic or coordinative bonds and a large variety of surface properties have been successfully demonstrated.

Generally there are two strategies to attach a desired functional group onto a substrate surface. Either you synthesize the whole molecule prior to adsorption or you use of a twostep approach by which the surface is first primed with a precursor monolayer which is subsequently transformed by in-situ surface reactions to the desired composition or coupled with an overlayer carrying the desired surface functionality. They both have their advantages and disadvantages and which strategy to choose depends completely on the system.⁵²

The main advantage in using the pre-synthesis approach is that the synthesis, purification and characterizations of the desired SAM-forming molecules can be completed in a controlled manner using standard methods. A 2 step approach is more complex and chemical reactions that work perfectly in solution might be completely inactive on the surface. Because of very limited possibilities for purification reaction side products should be avoided and a 100% reaction yield is required to prevent unreacted sites to be present on the surface⁵².

However the pre-synthesis approach has several disadvantages. It demands more synthetic efforts and because of incompatibilities between the desired SAM forming molecules and the adsorption protocol the approach might be impossible. In the pre-adsorption approach, a reactive anchor layer is attached to the surface in a step-wise fashion and often commercially available compounds can be used, thereby enabling a large variety of interfaces to be prepared with limited efforts. However, most problems with pre-adsorbed molecules occur because of incompatibilities between the desired molecule and the attachment procedure. It can be that the reaction conditions which might be very harsh destroy the functionality or that the functionality interferes with the monolayer formation. An example of a case where the functionality is very sensible to the reaction conditions is the adsorption of proteins in biosensing application. The proteins are required to remain folded with the biological functions intact which restricts the reaction conditions (temperature, solvent etc.) to a very narrow range which might seriously hamper the adsorption. In addition to the incompatibilities with the modification protocol, the desired functional SAM-forming molecules might be too bulky to allow a perfect coverage of the surface, hence preventing the formation of a monolayer with the desired quality⁵².

1.4.2. Organosilane monolayers on native, oxide-covered silicon

Since the pioneering work of Sagiv et. al.⁵³, studying the adsorption of long-chain trichloroand trimethoxy silanes on oxidic surfaces, this class of compounds has been the by far most studied system to functionalize silicon surfaces. The monolayer forms via a condensation reaction between the hydrolyzed trichloro- or trimethoxysilane and the hydroxyl groups of the oxide surface (Fig 1.6). As silicon in open atmosphere is always covered with a thin, native oxide layer, this protocol is very suitable for the functionalization of silicon surfaces. During the past 30 years of intense research on these monolayers, the reaction mechanism has been frequently debated and conflicting results have repeatedly been reported. Although the monolayer preparation protocol is simple for reproducible, high quality monolayers a number parameters such as precursor concentration, solvent, temperature, deposition time, water content and age of the adsorbate solution have to be carefully chosen, since small deviations may result in very different qualities of the monolayers^{54–56}. Water seems to play a major role in the condensation reaction affecting the order, the kinetics and the growth mechanism. Exposing oxidized silicon surfaces to organo silanes at moderate temperatures in water containing organic solvents, will result in an islands monolayer growth where the silanes are believed to react with the water and aggregate in solution before it binds to the silicon substrate⁵⁷. Monolayers formed at high temperatures tend to give a less densely packed film and favours homogeneous growth over islands growth. A critical temperature T_c has been observed where the transition between island growth and homogeneous growth occurs. Temperatures below T_c favour island growth and temperatures above T_c favour homogeneous growth. T_c is correlated to the chain length. Increasing the chain length increases T_c, hence short chain organo silanes tend to grow homogeneously and result in a less densely packed and more disordered film compared to long chain compounds⁵⁸.

Monolayer growth in water-free environments seems to proceed slowly and results in less densely packed monolayer, however the growth of islands has been observed even under these conditions.

Organo silanes are oriented almost parallel to the surface normal, tilted by only 8-10°, which makes them very similar to Langmuir-Blodgett films. The monolayers are also remarkable stable and survive in boiling water and organic solvents and are also quite resistant to acid solutions.



Figure 1. 6. Monolayer formation of trichlorosilanes adsorbed on silicon substrate covered with a native oxide.

However, there are also several disadvantages with this modification protocol and its implementation for the fabrication of molecular devices. A dielectric oxide layer separating the organic functionality and the silicon substrate will decrease the electrostatic response in sensor applications and cause fluctuations in electronic devices. Sensor responses are also highly affected by the presence of interface traps often appearing at oxide surfaces decreasing its efficiency even more. Other major obstacles are the sensitivity of these organosilane monolayers to basic solution, resulting in fast degradation of the monolayer. This prevents pH sensing and sensing in alkali solutions⁵⁴. Silicon oxide is also known to destabilize photoluminescence in porous silicon and thereby preventing such monolayers to

passivate the surface for such applications⁵⁹. Moreover, the unstable PL properties of lightemitting PSi are believed to be mainly due to the generation of nonradiative recombination centers at the initially H-terminated Si surface upon oxidation during air exposure or photooxidation⁵⁹. Despite these drawbacks, condensation of trichloro silanes onto oxide surfaces is one of the most reliable ways to form well packed monolayers and by adding a terminal functionality, functionalized silicon surfaces for various applications have been achieved⁵⁴

1.4.3. Si-C bonded monolayers on oxide free silicon surfaces

Several different approaches are known today to form monolayers that are directly, without an intermediate oxide layer, bonded to a silicon surface (Fig 1.7.). These monolayers are generally very stable owing to the strong Si-C surface bonds and avoid all the problems caused by the presence of the intermediate SiO₂



Grignard reagents functionalization

Figure 1. 7.. Different approaches to form Si-C bonded monolayers

Hydrosilylation

Among the methods to attach organic molecules to oxide free silicon surfaces under formation of a covalent Si-C bond, the hydrosilylation reaction of alkynes or alkenes on H-terminated silicon surfaces is probably the most versatile and best studied route (Fig. 1.8). Typically, to initiate the reaction between a hydrogen terminated surface and a terminal alkyne or alkene, heat or UV light are employed but also visible light and sonication⁶⁰ has been reported.



Figure 1.8. Hydrosilylation between a hydrogen terminated silicon surface and an alkyne or an alkene

The mechanism of this reaction is still controversial and seems to depend on the type of activation employed. The thermally activated hydrosilylation mechanism is probably the least debated and is generally accepted as a radical chain propagation (Fig. 1.9a). The initial step is a thermal cleavage of a Si-H bond, forming a silyl radical at the hydrogen-terminated silicon surface, known as a dangling bond. The silyl radical then attacks the alkene or alkyne resulting in a new covalent Si-C bond and a migration of the radical to the β -carbon atom. Subsequently one hydrogen atom is abstracted from a neighbouring Si-H bond at the hydrogen terminated silicon surface resulting in a Si-C bonded alkyl or alkenyl group and a new dangling bond at the silicon surface. This dangling bond can then react with another hydrocarbon chain and in this way the monolayer formation propagates across the surface⁶¹. Using deuterium terminated silicon surfaces, this mechanism has been experimentally confirmed on different silicon substrates such as flat silicon, porous silicon⁶², SiNWs and SiNPs⁶³ and theoretical studied using DFT calculations⁶⁴. The latter DFT study indicated that due to a lower H-abstraction energy barrier and a larger overall reaction enthalpy the reaction with terminal alkynes should be faster than with corresponding alkenes and should also lead to a more stable organic overlayer. This was later experimentally confirmed by two independent studies by Ciampi et.al 65 and Scheres et.al. 66 Typical reaction conditions for

thermally induced hydrosilylation reactions are neat alkyne/alkene at temperatures above 160 °C, a reaction time of at least 3h and and rigorous exclusion of oxygen. Hydrosilylation on porous silicon seems to demand less harsh reaction condition compared to flat silicon and has been successfully carried out in refluxing toluene at 110 °C⁶².

For photo-initiated hydrosilylation reactions, four mechanisms have been proposed (Fig. 1.9): (i) Si H bond homolysis followed by a radical reaction as described above (ii) photoemission: Photo induced electron emission followed by a nucleophilic attack on the positively charged silicon and hydrogen migration (iii) plasmon-mediated and (iv) exciton-mediated initiation: A valence band electron is excited to the conduction band and is stabilized through coulomb interaction with the formed electron hole in the valence band ⁶¹



Figure 1. 9. Hydrosilylation reaction mechanisms proposed by Buriak and co-workers (Scheme taken from Ref 61)

The mechanisms proposed for UV-initiated hydrosilylation are Si-bond homolysis and photoemission. Visible-light induced hydrosilylation is in addition to photoemission proposed to involve the formation of plasmons or quantum-confined exciton. The radical chain reaction is not likely to happen, since visible light has insufficient energy to break the Si-H bond. The mechanism of white-light initiated hydrosilylation reactions seems to follow a different route compared to UV or thermal initiation and proposals involving both plasmons and excitons have been presented. A result strongly in favour of the exciton mechanism is that efficient white-light adsorption has only been observed on photoluminescent, porous silicon. As

photoluminescence originates in the recombination of excitons, this is a strong indication supporting the exciton hypothesis.

Si(111) surfaces are in general easier to functionalize than Si(100), independent of the functionalization strategy. The reason for this is the higher surface roughness of Si(100) disturbing the monolayer formation and its more rapid oxidation making it more sensitive to unwanted oxygen in the reaction vessel.

Grafting of diazonium salts

In addition to the hydrosilylation reaction one promising way to functionalize oxide-free silicon surfaces with an organic layer is through electrochemical deposition of diazonium salts carrying the desired functionality (Fig 1.7). This method is very interesting because it can be used to modify a large variety of surfaces in addition to H-terminated silicon such as oxidized silicon⁶⁷, carbon, gold, platinum and more⁵². Thin films with a broad variety of functionalities have been prepared and the grafting can be carried out in aqueous as well as non-aqueous environments. The diazonium salts are relatively easy to prepare and the functionalized aromatic groups could be further modified by classical chemical reactions. However, packing densities and monolayer qualities are, in general, not as good as with other adsorption protocols.

Reactions with halogen terminated surface

Silicon surfaces can also be functionalized by reaction of a Grignard reagent (R-MgX) carrying the desired functionality with a halogenated silicon surface, prepared in the gas phase under UV-irradiation⁶⁸ or in solution phase by reaction with PCl₅⁶⁹ An almost 100% surface coverage was obtained when methyl groups were introduced using this approach, resulting in an excellent protection against oxdiation^{37,69}. However, this Grignard reaction is essentially limited to alkyl substituents with few options for further functionalization, hence limiting its practical applicability. Other drawbacks associated with this strategy are the hazards of Grignard reagents and the two step modification procedure instead of a direct one step modification in the hydrosilylation approach.

Pros/Cons Si-C bonded monolayers

The above described modification protocols for organic monolayers directly bonded onto bare silicon surfaces through Si-C bonds avoid many problems associated with organosilane

monolayers on oxide-covered silicon. There is no insulating layer separating the desired organic functionality from the surface, the monolayers are very stable also in alkaline solutions, there are no interface traps destroying photoluminescent properties. A variety of approaches including thermal, ultraviolet and visible light hydrosilylation, electrografting of diazonium salts and Grignard reactions leaves many options to adapt the adsorption conditions to the specific, required surface functionalities. Many reports in the literature have proven successful covalent grafting of a large variety of functionalities either through presyntheses adsorption or through multi step attachment procedures. Reactive H-terminated silicon surfaces can relatively easy be prepared through etching of the native silicon oxide layer in HF. Due to steric reasons, monolayers of long chain hydrocarbon yield a maximum coverage of about 50% of the reactive Si-H sites. In spite of that, its oxidation protection and electrical insulating properties are excellent⁷⁰. However, several fundamental questions are still unanswered, for example the conflicting results about the different adsorption mechanisms, the optimal conditions of the functionalization or the influence of the substrate morphology on monolayer formation and monolayer properties.

2. Characterization methods

As described in the last chapter, there are large amount of options to functionalize silicon surfaces with self assembled monolayers. However, once you have decided which approach that suits the system best, another great challenge remains, its characterization.

Method	What is	Information	Complexity	Advantages	Disadvantages
	measured?	yielded			
Contact angle	Surface energy	Expected hydro (or solvo) phobicity; Small hysteresis (indicates homogeneity)	Low	Simple, fast, sensitive. non- destructive	Contamination- sensitive
Elipsometry	Thickness	Layer thickness Refractive index	Low	Simple, fast, non- destructive, non contact.	Contamination sensitive,
FTIR	Molecular vibrations	Chemical composition profile. Packing density Molecular orientation;	Medium	Fast, non- destructive, Chemical and structural information	Contamination sensitive, Insensitive to some, vibrations/ orientations
XPS	Core levels	Elemental composition, chemical state, impurities	High	Detects elements; Quantitative down to % of monolayer	Destructive, Limited extraction of vertical profile, slow, expensive
AFM	Microscopic height & Position	Surface topography, surface structure (periodic and non-periodic	High	Sub- microscopic lateral and depth information	Limited integration capability, tip dependence

Table 2.1.	Overview	of monolaye	er characterization	methods45

The above mention techniques (table 2.1) were employed in this thesis to characterize self assembled monolayers. These techniques provide detailed information for characterizing monolayers and monitoring surface reaction. The most important informations for this thesis were extracted from contact angle measurements, ellipsometry and FTIR, hence these 3 methods are described in more detail in this chapter. However, in addition to the methods in

table 2.1 there are a plethora of other techniques that in the literature are frequently used to characterize monolayer (table 2.2.).

Experimental technique	Information that can be obtained		
Electronic	techniques		
Auger electron spectroscopy (AES)	Surface elemental composition, growth mode,		
	Coverage		
X-ray photoemission spectroscopy (XPS)	Elemental composition, chemical state, impurities		
Ultraviolet photoemission spectroscopy (UPS)	Valence band, density of occupied states,		
	bonding nature, band dispersion		
X-ray absorption near edge spectroscopy	Conduction band, density of empty electronic		
(XANES)	states, molecular orientation, bonding nature		
High-resolution electron energy loss	Adsorbate vibrations, phonons, adsorption sites		
righ-resolution electron energy loss			
spectroscopy (HREELS)			
Structural	techniques		
Extended x-ray absorption fine structure	Structural parameters. Atomic distances,		
(EXAFS)	molecular		
	Orientation, thermal vibrational amplitudes.		
	Coordination number		
Programmed thermal desorption (TPD)	Adsorption energies and site		
Low-energy electron diffraction (LEED)	Surface symmetry, atomic distances, molecular		
	orientation, thermal vibrational amplitudes		
V row differentian (VDD)	(needs periodicity)		
A-ray diffraction (XRD)	Crystal structure, atomic distances, molecular		
Grazing incidence x-ray diffraction (GIXD)	periodicity)		
	degree of order or crystallinity		
Ion scattering spectroscopy (ISS)	Surface structure and composition. H detection		
Time of flight direct recoil spectroscopy (TOF-			
DRS)			
Infrared spectroscopy (IR) Infrared reflection-	Specific chemical groups, adsorption site,		
absorption spectroscopy (IRAS)	surface orientation		
Surface plasmon enhanced Raman spectroscopy	Adsorbate vibration, surface phonons, molecular		
	tilt		
Atom scattering/diffraction	Surface structure		
Sum frequency generation (SFG)	Adsorbate vibrations, surface coverage,		
	conformation of		
	alkyl chains, adsorbate-substrate bond		
X-ray standing waves (XSW)	Bond distance, adsorption site		
A-ray reflectivity (XRR) (and also Neutron	Surface normal relaxations, surface roughness,		
reliectivity, NR)			
IVIICIOSCOPIC TECHNIQUES			
	surface structure (periodic and non-periodic)		
Atomic force microscopy (AFM)	Surface topography		
	surface structure (periodic and non-periodic)		
Scanning tunnelling spectroscopy (STS)	Local electronic states.		
	single molecule conductance		

 Table 2.2. Surface science techniques for characterization of SAMs.⁷¹

2.1. Ellipsometry

Ellipsometry is a fast and simple method that is generally used to determine the optical properties and thickness of different materials by detecting changes in light polarization caused by reflection or transmission from the material. Important advantages with ellipsometry is the easy, fast and non-destructive measurement procedure providing the optical properties of the material and reliable film thicknesses down to 0.1 nanometer at sample areas as small as 1 mm².

Light travelling through space can be described as an electromagnetic wave with an electric field orthogonal to the direction of propagation. Light from a source such as He/Ne is unpolarized which mean that the orientation and phase of the electric field is completely random oriented. The light will be linearly polarized when the two oscillating orthogonal light waves are in phase (fig 2.1). If the orthogonal waves are 90° out-of-phase and equal in amplitude, the resultant light is circularly polarized, elliptical polarization occur if orthogonal waves of arbitrary amplitude and phase are combined

By elipsometric measurements, Monochromatic light travels through a filter that polarize the light linearly, as the linearly polarized light is reflected from a surface, the phase and amplitude of the electric waves changes, resulting in an elliptically polarized beam The now elliptically polarized light is passed through a second polarizer, called the analyzer, that again polarize the light linearly and the light intensity is subsequently detected by the detector as a function of the angle of the analyzer. The phase and amplitude change (tan ψ) and the phase difference (Λ) are analyzed to extract the optical properties of the material yielding information such as the refractive index, the film thickness and surface roughness.



Figure 2.1 Schematic illustration of the construction of an ellipsometry

2.2. Contact angle Measurements

Information about surface energy, surface roughness and surface heterogeneity can be obtained by measuring the angle at which a liquid vapour interface meets a solid surface ^{72,73} Contact angle measurements is then a powerful tool to characterize self assembled monolayer as the measurement is fast, non-destructive and the obtained surface free energy varies widely with the types of functional groups on the surface. For hydrophobic surfaces, the free energy decreases in the order -CH₂>-CH₃>-CF₂>-CF₂H>-CF₃⁴⁰, making the contact angle sensitive to surface reactions and structural changes of the monolayer. For a self-assembled alkyl monolayer adsorbed on the surface, well-ordered monolayer will expose the CH₃-groups with a different surface energy than CH₂-gróups exposed in a disordered monolayer. Perfectly ordered alkyl monolayers adsorbed on flat surfaces generally generate a water contact angle of 109°-111° whereas defects immediately decreases this angle, hence providing information about the monolayer quality

There are various ways to carry out contact angle measurements, one common method is the sessile drop approach, there a liquid drop will be advanced very slowly over the surface via a syringe mounted above, and the contact angle θ is subsequently measured with a goniometer. If the substrate has an attractive force on the liquid the drop will wet the surface at a relatively large contact area. If contrariwise the force between the surface and the liquid is repulsive, the liquid will have a small contact area, hence a large contact angle is recorded. Generally you say that liquids with contact angles below 90° are wettable or lyophilic whereas surfaces with larger contact angles are dewetting or lyophobic.



Figure 2.2 Contact angle of a liquid droplet wetted to an ideal solid surface.

The contact angle of a liquid drop on a solid surface is defined by the molecular interactions across the liquid/vapour, solid/vapour, and solid/liquid interfaces. The relation between them is known as the Young's equation:

$$\gamma_{l\nu}\cos\theta_{Y} = \gamma_{s\nu} - \gamma_{sl} \qquad 2.1.$$

where θ is the measured contact angle, $\gamma_{l\nu}$ is the free surface energy of the liquid in contact with vapour, $\gamma_{s\nu}$ is the free surface energy of the solid in contact with vapour and γ_{sl} is the free surface energy of a solid covered with liquid. Young's Equation contains only two measurable quantities, the contact angle θ and the liquid–vapour surface tension, $\gamma_{l\nu}$. To determine $\gamma_{s\nu}$ and γ_{sl} from contact angle measurements, a couple of models are available, such as the Neumann Model⁷⁵ or Owens-Wendt-Rabel-Kaeble model (OWRK)⁷⁶.

Micro and nano structures on the surface have a strong influence on the wettingproperties and the Young equation isn't valued on such surfaces. There are two major types of mechanisms that explain the effect of roughness on the apparent contact angle of liquid drops, known as the Wenzel Model and the Cassie-Baxter model⁷⁷. These can be described as

$$\cos \theta c = r(\gamma_{SV} - \gamma_{SL})/LV = r \cos \theta \qquad \text{Wenzel Model} \qquad 2.2.$$

and
$$\cos \theta c = f_1 \cos \theta_1 + f_2 \cos \theta_2 \qquad \text{Cassie-Baxter (CB)} \qquad 2.3.$$

were θ_c is the contact angle, θ is the contact angle on flat surfaces, the r is the roughness and f_1 and f_2 are the projected area fraction of the liquid and the air



Figure 2.3. Young model, Wenzel model and Cassie-Baxter model

Wenzel characterized rough surfaces by a roughness ratio factor "r" defined as the ratio of the true area of the solid surface to its projection i.e., $r = A_{rough}/A_{flat}$ Adding the roughness

ratio factor "r" in Young's equation (γ_{SV} becomes $r\gamma_{SV}$ and γ_{SL} becomes $r\gamma_{SL}$) gives the Wenzel equation, The Wenzel Model assumes that the liquid wets all of the rough surfaces, and the equation immediately suggests that the increased total surface area geometrically enhances hydrophobicity, θ >90 and hydrophilicity for θ <90 ⁷⁸ as illustrated in fig 2.4.



Effect of Substrate Roughness on Contact Angle (WENZEL model)

Figure 2.4. The contact angle for a defined θ as a function of surface roughness calculated with the Wenzel equation.

The next model, the Cassie-Baxter Model, describes the presence of a heterogeneous solid surface that has domains with different surface free energies. This model considers the interface composed of two types of domains: fraction f_1 with contact angle of θ_1 , and fraction f_2 with contact angle of θ_2 where f_1 + f_2 =1. If one of the 2 components is air with a contact angle of 180° the Cassie-Baxter equation can be simplified as

$$\cos \theta c = f(\cos \theta + 1) - 1$$
 2.4

In contrast to the Wenzel relation, the Cassie relation allows of $\theta c > 90^\circ$, even with $\theta < 90^\circ$ if f are small, fig 2.5.



Effect of substrate porosity (1-Φs) on contact angle (CASSIE Model)

Figure 2.5. The contact angle for a defined θ as a function of surface roughness calculated with the Cassie-Baxter equation,

2.3. Infrared spectroscopy

A molecule can vibrate in various different ways, for a non-linear molecule with N atoms there are 3N-6 different vibrations, and depending of the art of vibration, the masses of the atoms involved and the strength of the bond, those vibrations oscillate at different frequencies. Smaller masses oscillate at a higher frequency because they are lighter and easier to move than larger masses. Deformation vibrations oscillate at lower frequencies compared to corresponding stretching because it is easier to bend a bond than to stretch or compress it. A molecular vibration is excited when the molecule absorbs a quantum of energy, corresponding to the vibration's frequency. Such vibration transitions typically require an amount of energy in the range of infrared radiation, allowing these vibrations, which are characteristic for functional groups, to be probed with infrared spectroscopy.

One of the greatest strengths of Infrared spectroscopy compared to other characterization methods is that it allows solid, liquid as well as gas phases to be characterized. For example, if the sample is a powder it can be finely grounded together with KBr, and subsequently measured in diffusion reflection or pressed into a thin disk to be measured in transmission. Liquid samples are often sandwiched between two windows (for example KBR) and measured in transmission. The spectrum is divided with a reference spectrum, containing only KBr, to remove unwanted background contributions in the sample spectrum.

Infrared spectroscopy is also an important tool in analysing thin films on surfaces due to the low cost, minimum sample preparation and the direct information about the surface composition that can be provided. Thin films on flat surfaces can be characterized with reflection methods such as Attenuated total reflection (ATR) and Reflection Absorption IR (RAIRS) or in transmission IR (TIR). Nanostructured surfaces such as porous silicon and silicon nanowire scatter the incident bream, hence characterized in diffuse reflection IR (DRIFT) or transmission IR (TIR).

2.3.1. Reflection Absorption Infrared Spectroscopy (RAIRS)

In Reflection Absorption Infrared Spectroscopy, the infrared beam hits the film in a defined incidence angle, passes through, is reflected at the substrate and passes the film again before it finally hits the detector. The absorption is commonly expressed as -log (R_s/R_0), where R_s is the sample (substrate plus adsorbate) reflectivity and R_0 is the reflectivity of a clean reference substrate. It is today a well-established technique for spectroscopic characterization of flat surfaces and provides information about the chemical composition as well as structural information such as the surface orientation of adsorbates. The interaction

between the infrared beam and the film is dependent on the direction of the oscillating electric field of the beam, the incident angle and the orientation of the molecular dipole moment. The electric field of the beam can be described by 2 separate components, one



Figure 2.6 Schematic illustration of the light in the RAIRS setup.

component oscillating parallel to the plane of incidence E_p and one component oscillating perpendicular to the same plane, E_s . The strongest absorption occurs when the electric field vector E is parallel to the orientation of the molecular dipole moment, T. On metals is the perpendicular component of the electric field almost entirely cancelled out due to destructive interference after a phase shift of nearly 180° upon reflection, hence vibrations perpendicular to the surface normal are inactive and will not be observed in a RAIRS spectra. The parallel component contrariwise reinforces and will interact with dipole moments parallel to the surface normal. This means that only vibrations with a component of the dipole moment oriented perpendicular to the metal surface will be absorbed which is commonly referred to as the metal surface selection rule. The intensity of the absorption bands are proportional to the strengths of the electric field, hence the most intense bands is provided at high incidence angles were the parallel component of the incoming electric field is almost perpendicular to the surface. The measurements are carried out with p-polarized light to eliminate noise caused by the inactive s.-polarized light.

On dielectric non-absorbing substrates such as silicon the situation is more complex because in contrast to metals the light is partly transmitted, the reflectivity is strongly dependant on the refractive index and an electric field exists both normal and parallel to the surface. This means that the surface metal selection rule is not valid on these substrates and both the parallel and the perpendicular component of the dipole moment contribute to the overall absorption. The existence of an electric field parallel to the surface allows s-polarized light to



Figure 2.7. a) Calculated reflectivity differences between the clean substrate (R_0) and an isotropic adsorbatecovered substrate (R_s) on a silicon surface. The solid line correspond to p-polarized light and the dashed to spolarized light. b) Calculated reflectivity differences between the clean substrate (R_0) and an isotropic adsorbatecovered substrate (R_s) on a gold surface In (c) calculated absorbances - log R_s/R_0 of the hypothetical adsorbate vibration at 3000 cm² on a silicon surface as a function of the light incidence angle p-polarized radiation The light are denoted with Ax and Az represent the parallel and perpendicular x z components, respectively, of the total absorbance Ap, and u B is the Brewster angle. The same optical constants as in (a) were used for substrates and adsorbate (Data taken from Ref 79)

be employed for spectroscopic surface characterization to detect surface vibration perpendicular to the surface normal and p-polarized light, having both a parallel and a perpendicular vector to detect both. In picture 2.7 published by Brunner et.al⁷⁹, calculated reflectivity differences between the clean substrate (R_0) and the adsorbate-covered substrate (R_s) illustrates that both R_0 and R_s on dielectric substrates depend strongly on the incidence
angle and polarization of the infrared radiation. A complex IR spectra is provided were the reflectivity change $R_0 - R_s$ upon absorption is not always positive, as one would expect as a consequence of light being absorbed by the sample, but can also due to an increase in reflectivity upon absorption be negative, resulting in inverted bands in the reflection spectrum. Absorption of S-polarized light will exclusively give such inverted bands with a maximum with angle of incidence below 60° whereas the reflectivity profile of p-polarized light is more complex and depended on the incidence angle and the orientation of the dipole moment since it interact both with perpendicular and parallel surface vibrations. The contribution of parallel and perpendicular vibrations to the overall band intensity is described in equation 2.4 and illustrated in fig 2.7 c from which can be concluded that their contribution to the intensity is in opposite direction^{55,79,80}.

$$I(\alpha) = -\left(\frac{R_s}{R_o}\right) = -k_1 \cos^2 \alpha + k_2 \sin^2 \alpha$$
 2.4.

2.3.2. Determining surface orientation with Reflection absorption infrared spectroscopy

The orientation of an ordered anisotropic uniaxial organic carbon chain in respect to the silicon substrate can be described by 3 angles as illustrated in figure 2.8. The angle α is the angle between the molecular backbone and the surface normal, the twist angle β describes the rotation of the hydrocarbon chain plane with respect to the molecular axis; and the angle of precession (ψ) describes the tilt direction³⁶. Most monolayer on most substrates have an isotropic oriented ψ described with the "magic angle", 54.7° and an 45° twist angle, which means that in most cases the tilt angle α is the only unknown parameter.



Figure 2.8. Long chain alkyne adsorbed on a Silicon substrate

A carbon chain adsorbed on a surface, exhibit 4 main stretchings in the 3000 region, 2 CH₂ absorptions at 2920 cm⁻¹ (v_{as} (CH₂)) and 2850 cm⁻¹(v_{s} (CH₂)) and 2 CH₃ stretchings at 2963 cm⁻¹(v_{as} CH₃)), 2872 cm⁻¹ (v_{s} (CH₃)). The direction of their dipolmoment is correlated to the tilt angle α , hence changing the tilt angle results in different absorbing band intensities and provides very different spectra. Using electromagnetic wave theory it is possible to simulate IR spectra as (-log(R_s/R₀)) of SAM with different orientation parameters until an acceptable fit between simulated spectra and experimental spectra is achieved, in this way can the surface orientation of the film be determined ^{55,79,81}. The exact procedure is described in ref [80] and in the experimental section.

3. Experimental

4.1 Chemicals and materials

Materials:

(100) oriented, N(Phosphorus)-doped, single-sided polished, 0.5 mm thickness, $1_5 \Omega$ cm resistivity) were purchased from Si-Mat Silicon Materials (Landsberg, Germany) were used for all substrates in this thesis.

Chemicals

Chemicals	Purity	Manufacture
DMF	99.9%	Sigma-Aldrich
DMSO	99.7	Sigma Aldrich
Ethanol	99.9	Merck
CCl ₄		
Sodium azide	99.99	Sigma Aldrich
Bromoctane	98%	Fluka
Ethyleneglycol, anhydrous	99.8%	Sigma Aldrich
Propiolic acid	95%	Sigma Aldrich
Dodecyne		ABCR
Pentadecyne		ABCR
1-Bromohexadecan		
Lithiumacetylide	90%	Sigma Aldrich
Ethylenediamine Complex		

Table 3.1 Used chemicals

3.2 Synthesis

Synthesis of adsorbate molecules

1-Octadecyne was synthesized according to a general procedure described previously ²⁹. 1-Bromohexadecane (15g, 49 mmol) was slowly added to a suspension of a lithium acetylideethylenediamine complex (6.5 g, 64 mmol) in dry DMSO (200 mL) at 0 °C under argon atmosphere. The mixture was allowed to warm to room temperature and held at r.t. for 12 h. Subsequently, water was carefully added, the resulting mixture was extracted with hexane (3x 200 mL), the organic phase was dried with NaSO₄, concentrated and distilled (bp. 110 °C, 4.5 x 10⁻² mbar) yielding the product (10.1 g, 82%) as a colourless liquid. IR (neat): 3319 (v(H-C=C)), (2929, 2857) (v(CH₂)), 2122 (v(C=C)), 1459 (δ (CH₂)), ¹H-NMR (250 MHz, CDCl₃): 0.83 (m, 3H), 1,1-1,6 (m, 28H), 1,9-2 (m, 1H), 2,1-2,3 (m, 2H)

1,2 Ethanediol-dipropiolate (EDDP) was synthesized according to a general procedure⁸². Ethylene glycol (10 mL, 0.1 mol) and propiolic acid (10.5 mL, 0.3 mol) were dissolved in toluene (100 mL). P-toluenesulfonic acid (4 g, 0.021 mol) was added and the solution was refluxed for 5 hours while continuously removing water via the water-toluene azeotrop (bp. 83 °C).The remaining solution was diluted with 300 mL toluene, washed with water, dried with anhydrous MgSO₄, concentrated and distilled (bp. 50 °C at 10⁻² mbar), yielding 14.1 g (86%) of EDDP as a colourless liquid. IR (neat): 3282 (v(H-C=C)), (2966, 2888) (v(CH₂)), 2122 (v(C=C)), 1717 (v(C=O)), 1453 (δ (CH₂)), 1212 (v(C-O)). ¹H-NMR (250 MHz, CDCl₃) : 2.98 (s, 2H), 4.4 (s, 4H).

Tetradecanolpropiolate (TDP) was synthesized from tetradecanol and propiolic acid according to the procedure described for EDDP. The crude were not distilled but recrystallized in Hexane forming the product as a colourless solid in 79 % yield. IR: 3231 (v(H-C=C)), 2966, (v(CH₃)), 2932,2856 (v(CH₂)), 2122 (v(C=C)), 1695 (v(C=O)), 1453 (δ (CH₂)), 1212 (v(C-O)). ¹H-NMR (250 MHz, CDCI₃) : 0.88 (m, 3 H), 1.25 (s, 23 H), 1.80 (m, 2H), 2.87 (s, 1H), 4.17 (t, J=6.5 Hz, 2H,)

1,2-Decadiol-dipropiolate (DDDP) was synthesized as EDDP from 1.2-decanediol and recrystallized in Hexane forming the product as a white solid in 75% yield. Mp = 38-40 °C IR (neat): 3282 (v(H-C=C)), (2966, 2888) (v(CH₂)), 2122 (v(C=C)), 1717 (v(C=O)), 1453

 $(\delta(CH_2))$, 1212 (v(C-O)). . ¹H-NMR (250 MHz, CDCI₃) : 1.30 (m, 12H), 1.86 (m, 4H), 2.8 (s, 2H), 4.19 (t, J=6.5 Hz , 4H,)

Pent-4-ynyl 3-(trimethylsilyl)propiolate

1-Pentynol (1.6 g, 19 mmol) and trimethylsilylpropiolic acid (2.8 g, 19 mmol) were dissolved in toluene, 20 mL . P-toluenesulfonic acid (0,36 g, 1.9 mmol) was added and the solution was refluxed for 5 hours while continuously removing water via the water-toluene azeotrop. The black liquid was purified on a column toluene gave the product in 0.4 g (10 % yield) as a yellow oil. 1.9 mmol

IR (neat):, (2966, 2888) (v(CH₂)), 2122 (v(C≡C)), 1717 (v(C=O)), 1453 (δ(CH₂)), 1250 (v(C-O)). ¹H-NMR (250 MHz, CDCI₃) :, 0.25 (s, 9 H), 1.97-1.85 (m 3 H), 2.35-2.30 (m 2 H). 4.3 (t, J = 6.5 Hz, 2H)

Synthesis of azides

Azides were prepared from corresponding bromine following a literature procedure for the analogous C12 compound³³.

1-azidooctane: The preparation of 1-octanazide describes a typical reaction. NaN₃ (12.1 g, 0.18 mol) was stirred in 80 mL dried DMSO for 1 hour whereupon 1-bromooctane (20 g, 0.1 mol) in THF (300 mL) was added. The mixture was stirred for 2 days, diluted with H₂O (100 mL), extracted with Et₂O (3 x 150 mL), washed with H₂O (3 x 100 mL) and concentrated, yielding 1-azidooctane (14.2 g, 90%) as a colourless liquid. IR (neat): 2958 (v(CH₃)), (2925, 2855) (v(CH₂)), 2098 (v(N=N=N)), 1464 (δ (CH₂)) ¹H-NMR (250 MHz, CDCl₃) : 0.86 (t, 3H), 1.2 (m 10 H) 1.58 (q 2 H), 3.25 (t, 2 H).

1-azidopentadecane: 81% yield, IR: 2956 ($v(CH_3)$), (2929, 2854) ($v(CH_2)$), 2096 (v(N=N=N)), 1464 ($\delta(CH_2)$) ¹H-NMR (250 MHz, CDCI₃) : 0.86 (t, 3H), 1.2-1.6 (m, 26H), 3.3 (m, 2H)

Cyanooctaneazide: 60% yield IR (neat):(2975, 2938, 2878) (v(CH₂)), 2249 (C≡N), 2115 (v(N=N=N))

1-(azidomethyl)-4-isocyanobenzene: The compound were in addition distilled, 86-90°C at 4x10⁻² mbar. IR(KBr): 3066 (Ar), 2237 (C≡N), 2117 (v(N=N=N)), 1479, 1281 ¹H-NMR (250 MHz, CDCl₃) : 4.47 (s, 2H), 7.50.-7.55(m 4 H)

1,3-Diazidopropane

1,3-Diazidopropane was prepared from 1,3-dibromopropane and NaNO3 according to a literature procedure⁸³. In brief, 1,3-dibromopropane (10.0 g, 49.6 mmol) was dissolved in N,N-dimethylformamide (160 mL) whereupon sodium azide (10.0 g,153.8 mmol) was added while stirring under argon. The reaction mixture was heated to 65 °C and stirred for approximately 60 h under argon. The reaction mixture was allowed to cool to room temperature and then diluted with diethyl ether. The obtained suspension was washed with water (3 x 200 mL) and brine (2 x 200 mL) and then dried over NaSO4. Filtration and evaporation gave a pale yellow liquid. (4.9 g, 76%). ¹H NMR (250 MHz, CDCl3) δ : 1.79-1.85 (m, 2H), 3.40 (t, J = 6.4 Hz, 4H).

Copper free Azide-alkyne cycloaddition (solution)

Ethane-1,2-diyl bis(1-octyl-1H-1,2,3-triazole-4-carboxylate)

EDDP (3g, 18 mmol) and 1-octaneazde (5.5 g, 36 mmol) were dissolved in ethanol and stirred under reflux for 15 h. The formed solid was separated from the solution through filtration and washed with ethanol, ether and hexane to remove any starting material. The 1,4 substituted triazole was formed in 6.6 g, 79% yield. ¹H NMR (250 MHz, CDCl3) $\overline{0}$: 8.08 (s, 2H), 4.7 (s, 4H), 4.4 (t, 4H), 1.9 (m, 4H) 1.3-1.25(m, 18H), 0,87 (t, 3H) ¹³C-NMR (250 MHz, CDCl3)): 160.5, 139.9, 127.8, 63.1, 51.0, 63.1, 51.0, 32.1, 30.4, 29.1, 26.6, 22.7, 14.2 IR(KBr): 3121 (C-H), 2961 (CH3), (2925, 2852) (CH2), 1720 (C=O), 1520, 1460 (CH2), 1383

3.3 Substrate Preparation

Oxide etch of flat substrate

Si wafers were cut into 18 mm x 25 mm pieces and were cleaned by wiping them with an ethanol soaked towel followed by sonication in ethanol for 3 min and UV-ozone oxidation for 10 min in a commercial UV-ozone cleaning chamber (Boekel Industries). The remaining native oxide layer was removed by 2 min etching in 5% HF, and subsequently rinsed with distilled water and ethanol and blow-dried with high purity nitrogen.

Porous Silicon preparation

Porous silicon were prepared on commercial silicon wafers by stain etching following a general recipe by Abramof et al⁸⁴. Si wafers were cut into 20 mm x 25 mm pieces and were cleaned by sonication in ethanol for 3 min followed by UV-ozone oxidation for 10 min in a commercial UV-ozone cleaning chamber (Boekel Industries). The remaining native oxide layer was subsequently removed by 2 min etching in 5% HF. The samples were washed with distilled water and transferred into a HF/HNO3 etchant in a volume of 500:1 and etched for 10 min. Small amount of NaNO₂ 0.1 g/ I was added to the etch solution in order to homogenize the stain

etching, After the etching the samples were rinsed in water and ethanol and blow-dried with high purity nitrogen.

Silicon nanowire preparation.

Silicon nanowires were prepared on commercial silicon wafers by silver-catalyzed etching following a general recipe by Zhang et al.³⁴. Si wafers were cut into 20 mm x 25 mm pieces and were cleaned by sonication in ethanol for 3 min followed by UV-ozone oxidation for 10 min in a commercial UV-ozone cleaning chamber (Boekel Industries). The remaining native oxide layer was subsequently removed by 2 min etching in 5% HF, the samples were washed with distilled water and transferred into a Ag coating solution containing 5 mM AgNO₃ and 4.5 M HF in water, where they were left for 1 min under slow stirring. Afterwards they were washed with water to remove excess Ag and were immersed in an etching solution containing 4.8 M HF and 0.4 M H_2O_2 in water for 30 min in the dark. The samples were rinsed with water and finally immersed in 33% HNO₃ to dissolve the deposited Ag catalyst, The sample were subsequently rinsed with distilled water and ethanol and were blow-dried with high purity nitrogen (99.999%). A homogeneous black surface of densely packed and uniformly oriented nanowires was reproducibly obtained following this procedure.

3.4. Chemical modification of silicon substrates

The following step were carried out to chemically modify the silicon substrate

- Cleaning and oxide etching (removal of contaminants and of the native oxide forming a hydrogen terminated surface)
- 2) Hydrosilylation with alkynes in exclusive moisture and oxygen free environment to form an alkenyl monolayer
- 3) Removal of physisorbed molecules
- 4) Post modification via click chemistry

Oxide etching

Oxide etching of silicon wafer:

Oxide etch of silicon wafers were carried out as previously described, the freshly etched wafers were immediately used for further characterization and functionalization.

Oxide etch of porous silicon:

Porous silicon were cleaned by sonication in ethanol for 3 min and subsequently immersed in a in piranha solution (95% $H_2SO_4/30\%$ H_2O_2 4:1 v/v) for 30 min, rinsed with water and immersed in 5% HF solution for 5 min to remove the native oxide and create a H-terminated surface.

The etched substrates were rinsed with water and ethanol and blow-dried with nitrogen gas and immediately used for further characterization and functionalization..

Oxide etch of silicon nanowire

Silicon nanowires were placed in piranha solution (95% H₂SO₄/30% H₂O₂ 4:1 v/v) for 30 min, rinsed with water and immersed in 5% HF solution for 5 min to remove the native oxide and create a H-terminated surface of the nanowires. The nanowire wafer were rinsed with water and Ethanol, blow-dried in nitrogen and immediately used for further characterization and functionalization.

Alkyl monolayer preparation

The hydrosilylation reaction conditions are the same for all substrate (silicon wafer, porous silicon, silicon nanowire) but varies depending on which alkyne that is adsorbed. The exact reaction conditions are outlined in table 3.2.

Alkyne	Temperature (°C)	Concentration (M)
n-Alkynes	170°C	Neat alkyne
Dialkynes	170°C	Neat alkyne
Propiolic acid	120°C	0.2 M (mesitylene)
Propiolate esters	120°C	0.2 M (mesitylene)
(pent-4-ynyl 3-	150°C	0.2 M (mesitylene)
(trimethylsilyl)propiolate)		

Table 3.2. Reaction condition for adsorption of n- alkynes

The freshly etched silicon wafers were immersed into homemade flask (fig 3.1) containing a flask, and reflux condenser with neat alkyne or alkyne in mesitylene, which had been deoxygenated by a flow of argon for at least 1 h. Subsequently, the solution was heated by immersing the flask into a silicon oil bath and it was left over night maintaining a weak Ar flow. The flask was subsequently cooled to r.t and the sample was removed from the solution, rinsed and cleaned to get rid of physisorbed materials.



Figur 3.1. Reaction vessel used for hydrosilylation reactions

Removal of physisorbed molecules, silicon wafer

Removal of physisorbed molecules, silicon wafer:

Silicon wafer were cleaned by wiping them with a ethanol soaked towel followed by sonication in ethanol and toluene for 3 min. The wafer were subsequently rinsed with ethanol and blow-dried with high purity nitrogen.

Removal of physisorbed molecules, porous silicon:

Porous silicon were cleaned by sonication in ethanol and toluene for 10 min, rinsed and blow-dried with high purity nitrogen.

Removal of physisorbed molecules, silicon nanowire:

Since silicon nanowire breaks by sonication, they were cleaned in ethanol (50°C) for 1 h, subsequently rinsed and blow-dried in high purity nitrogen.

Post modification via click chemistry

Copper catalysed Huisgen azide-alkyne coupling:

Copper catalysed click reaction on porous silicon and silicon nanowires were carried out according to a slightly modified literature procedure⁸⁵. Briefly in a typical click reaction, alkyne-functionalized silicon surfaces were under R:T immersed into a solution containing the 1-azidooctane (20 mM), ethanol/water 1:1, copper(II) sulphate pentahydrate (5 mol % relative to the azide) and sodium ascorbate (25 mol % relative to the azide) and were kept there approximately 24h. The modified samples were rinsed consecutively with copious amounts of water, ethanol and toluene, were subsequently blow-dried with high purity nitrogen and then analyzed.

Copper free azide-alkyne cycloaddition:

The Si substrates were placed in a 0.2 M solution of the azide in Ethanol at 50°C for approximately 8h, was subsequently rinsed with ethanol and was blow-dried in nitrogen .

3.5. Infrared spectroscopy measurements

Infrared spectroscopy measurements were recorded on a Bruker Vertex 80 FT-IR spectrometer equipped with an external globar source and a narrow-band MCT detector and a TGS-detector.

FTIR measurements of solid substances

Solid chemicals were measured in diffusion reflection Infrared Fourier transformations (DRIFT). The solid substance (20mg) were diluted with KBr (500 mg) and subsequently finely grinded. The powder were mounted in a commercial variable-angle reflection unit (Seagull, Harrick Scientific) set at 15° incidence angle and were probed with unpolarized IR-radiation. 64 scans at 4 cm⁻¹ resolution were averaged from each sample and were ratioed against 64 scans from pure KBr. The IR were detected on a MCT detector.

FTIR measurements of liquid substances

Liquid substances were measured in transmission between two pressed NaCl plates The IR were detected on a TGS detector.

Transmission Infrared measurements of porous silicon and silicon nanowire.

Spectra of modified SiNW samples were measured in transmission at normal incidence. A native oxide covered Si sample, freshly cleaned in piranha solution, or a hydrogen terminated sample etched in 5% HF solution, were used as a reference. 1024 scans at 4 cm⁻¹ resolution were measured from sample and reference, and the resulting transmission

spectra were baseline corrected using the OPUS interactive baseline correction software supplied with the Bruker spectrometer.



Figur 3.2 Seagull reflection unit used for reflection IR measurements.

Reflection Absorption Infrared Spectroscopy (RAIRS) measurements of silicon wafers.

25mm x 18 mm silicon substrates were mounted in a commercial variable-angle reflection unit (Seagull, Harrick Scientific, fig 3.2) set at 81° incidence angle and were probed with p-polarized radiation obtained with a wire grid polarizer. 1024 scans at 4 cm⁻¹ resolution were averaged from each sample and were ratioed against 1024 scans from a clean, native silicon reference substrate.

Diffusion Reflection Infrared Fourier Transformation (DRIFT) measurements of structured Si substrates.

25mm x 18 mm silicon substrates were mounted in a commercial variable-angle reflection unit (Seagull, Harrick Scientific) set at 15° incidence angle and were probed with unpolarized IR-radiation. 1024 scans at 4 cm⁻¹ resolution were averaged from each sample and were ratioed against 1024 scans from a clean, native silicon reference substrate

ATR measurements

A Si ATR prism, 50x10x3 mm, 30 degree (Macrooptica Ltd) was mounted in a twin parallel mirror reflection attachment unit (TMP-220, Harrich scientific corporation) and was probed

with unpolarized IR-radiation. 1024 scans at 4 cm⁻¹ resolution were averaged from each sample and were ratioed against 1024 scans from a clean, native Si ATR prism reference.

Spectral Simulations

Spectal simulation were described in detail previously⁸⁰. Briefly, the sample is treated as a classical three-phase parallel slab model (air/monolayer/silicon). Air and silicon are assumed as semi-infinite, optically isotropic and non-absorbing (k=0) phases with a frequencyindependent refractive index of n(air) = 1 and n(Si) = 3.42 in the frequency range around 3000 cm⁻¹. Each monolayer is characterized by a thickness d (measured ellipsometrically) and an anisotropic dielectric function $\varepsilon(v,\xi) = [n(v,\xi) + j k(v,\xi)]^2$, which, for uniaxial symmetry around the surface normal, is a diagonalized second rank tensor and depends on both frequency v and spatial direction ξ . The monolayer absorption coefficient $k(v,\xi)$ for a certain, assumed molecule orientation in the monolayer is constructed, as previously described, from the isotropic absorption coefficients of a suitable reference compound (see below) and the internal coordinates of each vibration of the film molecules. The monolayer refractive index $n(v,\xi)$ is then obtained from $k(v,\xi)$ by Kramers-Kronig transformation. The Fresnel reflection coefficient rs (v) of the three-phase model is then calculated as a function of frequency based on classical electromagnetic theory, and by multiplication with the conjugate complex coefficient the R = r.r^{*} the sample reflectivity R(v) and the IR reflection spectrum for the assumed molecule orientation are obtained. The only fitting parameters in the present study were, for highly ordered films, the tilt angle α of the hydrocarbon chain axis with respect to the surface normal and, for partly disordered films, the relative percentage of ordered and disordered film domains. As the monolayers of a C_nH_{2n-2} terminal alkyne were assumed to consist of C_{n-2}H_{2n-3} alkyl groups attached to surface bound alkene (C₂H₂) units (Scheme 1), we used hexadecyl ($C_{16}H_{33}$) as the reference compound for octadecyne monolayers, tridecyl ($C_{13}H_{27}$) for pentadecyne monolayers and decyl ($C_{10}H_{21}$) for dodecyne monolayers. The corresponding spectral parameters for the CH-stretching absorptions (peak frequencies, absorption coefficients, absorption half widths) of these reference compounds are listed in Table 1 and were derived from a transmission IR spectrum of dioctadecyl disulfide under the assumption of constant, chain-length independent v(CH₃) spectral parameters and $v(CH_2)$ intensities linearly proportional to the number of CH₂ groups in the molecule.

vibration	peak frequency	band width (fwhm)	absorption coefficient		
	(cm ⁻¹)	(cm ⁻¹)			
			Hexadecyl	Tridecyl	Decyl
vas (CH3) ip	2962	12	0.030	0.030	0.030
v_{as} (CH ₃) $_{op}$	2950	10	0.023	0.023	0.023
v _s (CH ₃) _{FR}	2937	12	0.008	0.008	0.008
$v_{as} (\alpha \text{-} CH_2)^b$	2927	10	0.070	0.070	0.070
v _{as} (CH ₂)	2919	12	0.267	0.210	0.153
v _s (CH ₂) _{FR}	2906	11	0.025	0.020	0.015
v _s (CH ₂) _{FR}	2892	17	0.027	0.021	0.016
v _s (CH ₃)	2878	10	0.018	0.018	0.018
$v_s (\alpha$ -CH ₂) ^b	2860	16	0.015	0.015	0.015
$v_s (\beta \text{-}CH_2)^b$	2853	10	0.021	0.021	0.021
v _s (CH ₂)	2851	12	0.151	0.116	0.081

 Table 3.3. Spectral parameters for the CH stretching absorptions of different alkyl groups based on literature data for octadecyl⁵⁵

3.6. Ellipsometric measurements

Ellipsometric film thickness measurements were carried out on a Plasmos SD 2300 ellipsometer with a rotating analyzer and a He-Ne laser at 68°. Film thicknesses were calculated from the measured ellipsometric angles using the commercial instrument software. An optically isotropic three-phase system (bulk silicon phase 0, organic film phase 1, air phase 2) were used with literature values for the optical compounds of silicon (n=3.865, k=0.02) and a refractive index of 1,5 was assumed for the monolayer films (k = 0). Each sample was measured at 3 different spots on the surface and these values always lay within ± 1 Å.

3.7. Contact Angle measurements

Wettability changes of the treated surfaces are characterized by static contact angle measurements using the sessile drop technique. The measurements are performed at room temperature on a Krüss DSA 30 (Krüuss-Germany) using two different liquids, distilled water and ethylene glycol. The values of the contact angles shown in this thesis are the average of at least 3 measurements. The surface free energy was subsequently determined by the method of Owens–Wendt–Rabel-Kaeble method (OWRK) using the commercial instrument software supplied with the Krüss DSA 30.

3.8. NMR measurements

¹H and ¹³C NMR spectra were recorded on a Brucker Avance 250 (250.13 MHz {¹H}, 62.86 MHz {¹³C}) spectrometer. Chemical shifts are reported as δ values with TMS as standard.

4. Results and discussion

4.1 Preparation and properties of oxide-free planar (2D) and structured (3D) silicon substrates.

As it was shown in the section 1.2. functionalized, oxide free silicon substrates can be employed for a broad diversity of applications.

The first step to modify a silicon surface with organic compounds is the preparation of an oxide-free surface with the desired topography. In this section the preparation of oxide free planar silicon, porous silicon and silicon nanowire from Si(100) wafers are described.



Figure 4.1. Schematic illustration about the formation of H-terminated silicon substrate with different topologies.

There are many ways to prepare nanostructured silicon surface. The focus in this thesis lies in simplicity, methods that can be employed in any chemistry laboratory without the need of expensive equipments.

Three methods are described here, oxide etching of native silicon wafers in dilute HF solutions, anisotropic oxidative etching of silicon wafers to form a surface layer of porous silicon and metal catalysed etching of silicon wafers to form silicon nanowires.

4.1.1 Silicon (100) wafers

Bare silicon surfaces are highly reactive and rapidly form a native oxide layer with a thickness of several Ångström when exposed to the atmosphere. To remove this native oxide, the silicon is exposed to a dilute fluoride solution which dissolves the native oxide to hexafluororsilic acid. Generally Si(111) surfaces are etched in an ammonium fluoride etchant solution in order to form a perfectly flat surface, since HF is known to cause microscopically surfaces, Si(100) on he other hand, are etched in dilute HF for best homogeneous result since NH4F is known to etch Si(100) anisotropically and hence roughen the surface⁸⁶.

The oxide etching of Si(100) surfaces could be followed with a number of surface techniques, including water contact angle measurements, ellipsometry, AFM, and RAIRS (Table 4.1.). From these methods could be concluded that the oxide is etched away rapidly. Changes in wetting properties due to hydrogen replacing hydroxyl groups could be observed already after 20 s etching by an increase in water contact angle from <10° on oxidized wafers to approximately 85° on etched wafers. That is in good agreement with reported values on Hterminated silicon surfaces. The freshly etched hydrophobic wafers will strongly reject water, hence resulting in an almost dry surface when taking out from the HF solution. In comparison, oxidized hydrophilic surfaces are completely wetted by water. A slightly wet surface after etching is an indication of either incomplete etching or, more likely, surface contaminates. Ellipsometric measurements of the freshly etched silicon wafers showed a decrease in the oxide layer thickness from about 12 Å to 3 Å. This residual 3 Å layer should not be taken for oxide but is due to the internal roughness of the Si (100) wafer. The roughness could further be confirmed by AFM imaging by comparing etched wafers with Root-mean-Square (RMS) roughness of 0,1-0.2 nm compared to oxidized wafers that in comparison are perfectly flat. RAIRS spectra further confirmed silicon mono-, di-, and trihydride stretching.

SiO ₂	\Box	H H	H
Si	HF	Si	3 0

Method	Before etching	After Etching
Ellipsometric	12 Å	3 Å
Measurements		
AFM (RMS)		0.1-0.0.2 nm
FTIR	1242, 1052 v(SiO ₂)	ν(2085 cm ⁻¹) mono-,
		$v(2115 \text{ cm}^{-1}) \text{ di- and}$
		v(2142) tri-hydride
		stretchings
XPS	Si 2p, 104 eV (oxide peak)	No oxide peak

 Table 4.1 Characteristics of Si(100) before and after etching in 5% HF-solution

Exposing the silicon samples to the HF solution for a longer time than 20 s seems to have little or no influence on the wetting properties or the surface roughness as outlined in Table 4.2. We can thereby conclude that the silicon oxide rapidly dissolves and that the remaining H-terminated silicon surface is relative inert to dilute HF-solutions, although slowly roughening of the surface will appear with time.

Etching	Water	Oxide	AFM
time	Contact	thickness	(RMS)
	Angel		
0 min	<10	12	
20 s	79-84	3	
1 min	80-85	3	0.15
2 min	80-85	3	0.14
5 min	80-85	3	
10 min	80-85	3	0.18
30 min	80-85	3	
45 min	80-85	3	0.28

 Table 4.2 Etching of Si(100) wafer

4.1.2. Porous silicon

There are a number of methods available for anisotropic etching of silicon, including anodic etching, chemical stain etching, chemical vapour etching, laser-induced etching (LIE), metal-assisted etching, spark processing and reactive ion (plasma) etching. The by far most commonly employed method is anodic etching due to the superior properties of the resulting porous Si substrates (high photoluminescence efficiency, homogeneity, and reproducibility⁸⁷). In this work, porous silicon was prepared through stain etching in a HNO₃/HF etchant solution. This is a very easy and cheap way for porosification of silicon and despite its lower reproducibility compared to anodic etching it is a fast and simple alternative. The structure of stain etched, porous Si is similar to the one fabricated by the anodization method and the resulting pores are in the range of 1 nm up to the several micrometers .⁸⁷

Turner et.al^{87,88} proposed that there are anodic and cathodic sites on the surface of the semiconductor with local cell currents flowing between them. Hence the following mechanism is proposed, where m is the average number of holes required to dissolve one Si atom:

Anode:

$$\begin{split} \text{Si} + 2\text{H}_2\text{O} + \text{mh} + &\rightarrow \text{SiO}_2 + 4\text{H}^+ + (4 - \text{m})\text{e} - \\ \text{SiO}_2 + 6\text{HF} &\rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O} \end{split}$$

Cathode:

 $HNO_3 + 3H^{\scriptscriptstyle +} \rightarrow NO + 2H_2O + 3h +$

Overall:

 $3Si + 4HNO_3 + 18HF \rightarrow 3H_2SiF_6 + 4NO + 8H_2O + 3(4 - m)h^+ + 3(4 - m)e^-$

Etching silicon in a HF/HNO₃ solution generally requires a long induction period prior to the etching starts. To accelerate the induction time the stain HF/HNO3 etching is often assisted with NaNO₂. The importance of NaNO₂ was first noted by Schwartz et.al,⁸⁹. Turner et. al. subsequently proposed that the formation of HNO₂ which is easily generated in the presence of NaNO₂ is the rate determining step in silicon etching⁹⁰.

Porous silicon was prepared here in 40% HF and conc. HNO_3 in a volume ratio of 500:1 with a small amount of $NaNO_2$ (0.1 g/ I) added to the etch solution in order to homogenize and reduce the induction time⁸⁴. Immersing the silicon substrate in the etchant solution in the absence of $NaNO_2$ yielded very long etching induction times of more than 10 min. In the presence of $NaNO_2$ the etching generally started within minutes as could be confirmed simple by observing the sample. Small bubbles started forming on a narrow part of the silicon

surface immediately followed by a colour chance due to the nanostructures formed. The etching spreads within minutes to the rest of the surface, yielding a porous silicon layer with cavelike holes of about 1 um sizes (4.2).



Figur 4.2 SEM image of prepared porous silicon

4.1.3. Silicon Nanowires

As described in section 1.3. there are many possibilities to prepare silicon nanowires. In this thesis, they were prepared through metal-catalysed electroless etching²⁸. The principles and mechanism of this process is described in detail in section 1.3. of this work.

The process of silicon nanowire formation could easily be followed visually. The galvanic deposition of Ag onto the surface immediately results in a colour change, whereby the shiny grey metal colour of bare silicon wafers changes to blueish. For well ordered silicon nanowire to be formed in the subsequent etching step, it is important that the surface after Ag deposition has homogeneous dark blue colour. Inhomogeneous brighter surfaces that might be the result of surface contaminants will yield disordered, nonuniform nanowire arrays. The subsequent etching reaction starts immediately after exposing the Ag-covered substrate to the HF/H₂O₂ solution. Rather vigorous hydrogen evolution starts and the blueish surface changes to brown-yellow and eventually to black as the light absorbing nanowires are formed. Characteristic for a uniform, highly ordered silicon nanowire array is a homogenous

dark black surface. Brighter, yellowish surfaces indicate an array with less ordered nanowires of lower quality, which was confirmed with SEM-imaging (Fig 4.5.)



a) Yellow part

b) Black part

Figure 4.3. SEM images of inhomogeneous etched silicon nanowire on a silicon wafer. Image (a) is measured from a part of the wafer with a yellow appearance whereas image b is from a black part of the wafer. You can clearly see the correlation that black samples correspond to well aligned orthogonal silicon nanowire whereas a yellow colour indicates disorder and defects.

The formation of hydrogen gas during the etching contradicts the reaction mechanism proposed by Zhang et al²⁸ described in section 1.3 and favors the mechanism suggested by Zhu.et al¹³, where Ag only facilitates the silicon etching as the electron transport medium but does not participate in the reaction. The etching will then proceed through the current doubling mechanism (section 1.2.) producing hydrogen gas.

The lengths of the nanowires could be controlled by the etching time. High quality nanowires with a diameter of approximately 100 nm and a length ranging from a few micrometers up to over hundred micrometers were successfully prepared, using etching times between 10 min and 8 hours (Fig. 4.6). Etching times up to 25 hours resulted in nanowires about 180 μ m long (Fig. 4.5), however, the array of wires was of low quality, highly disordered and defect. In comparison, nanowires etched 5 min were partly bundled and the surface appeared dark brown but not dark black characteristic for well ordered silicon nanowire arrays. 10 minutes etching, on the other hand, gave an already perfectly ordered array of perpendicular

nanowires (Fig. 4.4.). The optimum etching times where highly ordered, perpendicual nanowires are formed, thus appear to lie between 10 min and about 8 hours.



Figure 4.4. Si nanowire etched 30 min giving homogeneous well aligned silicon nanowires



Figure 4.5. SEM images of electroless etched silicon 24 h and 5 min respectively. The wafer that is etched 24 h yields wires up to 180 um however it is a defect uneven nanowire array. Wafer etched only 5 min yields about 3 um long nanowires, however they are also defect and partly bundled.



Figure 4.6. Growth of silicon nanowire with metal catalysed chemical etching.

Also, the IR-transmittance of SiNWs in the mid-IR range strongly depends on the immersion time in the HF/H₂O₂ etching solution. Fig. 4.7a shows typical IR transmittance spectra of SiNW samples etched for 30 min, 60 min and 120 min, yielding nanowires with diameters approximately 100 nm and lengths of about 20, 40 and 60 μ m. The IR transmittance decreases strongly with increasing nanowire length and falls below 2% in the mid-IR range for 60 min etched wires. With respect to IR transmission measurements, an immersion time of 30 min, providing about 20 μ m long NWs, is the best choice in terms of spectral signal-to-noise ratio and provides an optimum between a high-enough sample transmittance and a sufficient sample surface area. Alternatively, IR spectra of SiNWs can als be measured in diffuse reflection. Analogous to transmission, also the diffuse reflectivity of the silicon nanowire array decreases strongly with etching times. Measurements of the diffuse reflectivity from three nanowire samples etched 30 min, 1 h and 2h are shown in Fig. 4.7b. and are quite representative for other samples.

As described in the literature⁹¹, we observe that silicon nanowires that are grown as a disordered arrays with the VLS technique have a dull yellow appearance, indicating that a large fraction of the incident light is reflected by scattering and not absorbed as in the case of black, ordered nanowire arrays. Also the reflectivity of infrared light differs between ordered and disordered NWs At 80 ° incidence angle the disordered silicon nanowire prepared via VLS reflected very IR radiation well, more than twice as strong as a flat silicon substrate. The reflectivity of ordered orthogonally aligned SiNWs, on the contrary, is lower than the blank wafer.

1



Figure 4.7. a) Transmission spectra of silicon nanowire etched 30 min, 1h and 2h min divided by the empty beam. b) Single beam DRIFT spectrum of nanowire etched 30 min, 1h and 2h executed at an incidence angle of 15°



Figure 4.8. Si-H stretchings on hydrogen terminated a) flat silicon measured in RAIRS b) porous silicon c) silicon nanowire both measured transmission.

RAIRS spectra of the chemically identical but structurally very different substrates Si(100) wafer, porous silicon and silicon nanowires are shown in Fig. 4.8 and evidence clear differences in the H-termination. Silicon (100) surfaces form a mixture of mono-, di- and trihydride stretchings with peaks at 2085 cm⁻¹, 2115 cm⁻¹ and 2142 cm⁻¹ and those were found on all three substrates. On SiNWs (Fig 4.8.c), the peaks are broad, inhomogeneous and overlapped; however, predominant are the mono- and dihydride absorptions whereas only a minor trihydride stretching peak appears. The trihydride peak is fairly symmetrical unlike both the mono and dihydride peak which exhibit at least one additional absorption seen as a shoulder of the main peak. As previously described in the literature⁹², the strongest monohydride feature at 2085 cm⁻¹ is likely to correspond to ideal Si-H whereas the shoulder at 2070 cm⁻¹ might be associated with an adatom structure (Si-H bonded to an adjacent SiH₂). The dihydride stretchings at 2102 cm⁻¹ and 2110 cm⁻¹ might be assigned to relaxed and strained dihydride and the relative broad trihydride band at 2142 cm⁻¹ might consist of a mixture of trihydrides in different environments.

Porous silicon (Fig 4.8.b) exhibits mono-, di- as well as trihydride absorpitons with the dihydride peak being predominant. However, the peaks are broader and extensively overlapped compared to the spectrum of silicon nanowires. It can therefore be assumed that the stain etched porous silicon surface is less ideally terminated by hydrogen because of the inhomogeneous non-ideal surface, involving Si-H groups of different stochiometry and in a variety of different environments, giving rise to a wide distribution of Si-H stretching absorptions..

IR spectra on planar silicon (Fig. 4.8.a) differ from the corresponding silicon nanowire and porous silicon spectra in that the monohydride band is hardly visible and the di- and trihydride peaks are much sharper although the dihydride absorption exhibits a weak shoulder. The absence of the monohydride peak may either be due to a vanishingly small surface concentration of this species or to its spectral invisibility based on the selection rules for RAIRS spectra (see section 2.3.1)

Summary

The described experimental procedures allow simple and cheap preparation of oxide-free hydrogen-terminated silicon surfaces with different topologies. Flat surfaces are simply exposed to dilute HF solutions in order to remove the native oxide. Anisotropic oxidative etching under formation of irregular pores were carried out in a HNO₃/HF etchant solution and high quality vertically aligned silicon nanowires were formed through Ag-catalyzed etching in HF/H₂O₂. Especially the possibility to form defect free silicon nanowire arrays, at low cost and in large scale is very interesting for new applications and it opens the field of nanoscience to any research group having access to a chemistry laboratory. As a consequence, we can expect a significant increase in publications dealing with silicon nanowires for a broad range of different applications.

4.2. Alkylation of silicon surfaces via hydrosilylation of n-alkynes

4.2.1. Thermal hydrosilylation on planar and nanostructured silicon substrates.

As previously described in section 1.4, adsorbing an organic monolayer directly onto an oxide free silicon surface will protect the surface against oxidation, and by attaching specific functional groups, unique properties can be employed allowing the modified substrate to be used in sensor^{18,19,30}, photovoltaic^{51,93} or catalytic³³ applications. Among a variety of methods to attach such organic molecules to oxide free silicon surfaces under formation of a covalent Si-C bond, the thermal-, UV- or white light initiated hydrosilylation reactions of alkynes forming alkene monolayer or alkenes forming alkyl monolayers on H-terminated silicon surfaces is probably the most versatile and best studied route.

In this thesis thermal hydrosilylation with alkynes were carried out. Hydrosilylation of Si(100) surfaces is more difficult than Si(111) due to its internal roughness and its lower resistance against oxidation. The hydrosilylation reactions is carried out at 170°C in neat alkyne and under complete exclusion of oxygen and water in order to get a well packed monolayer.

The formation of ordered monolayers on flat silicon wafers could be confirmed by an increase in water contact angle from about 83° to 109 ° which is in good agreement with ordered, long-chain trichlorosilane monolayer on native silicon or thiol monolayers on gold. Ellipsometric measurements also showed an increase in layer thickness in good agreement with theoretically predicted values. In addition, XPS measurements showed an increase in the carbon peak intensities and RAIRS measurements showed the characteristic CH stretching bands known from trichlorosilane monolayers on oxide-covered silicon, namely two positive CH₂ peaks at 2920 cm⁻¹ and 2850 cm⁻¹ and two negative CH₃ peaks at 2963 cm⁻¹ and 2872 cm⁻¹.

The structure of the monolayer has been much debated, primarily whether it is an alkyl monolayer or an alkenyl monolayer. In some studies alkenyl has been identified by a weak infrared C=C stretching absorption around 1600 cm-1^{94–96}, other reports could not detect this band⁹⁷, either because of insufficient sensitivity or because of a follow up reaction of the C=C double bond with a neighbour Si-H bond under the formation of a saturated double-bonded alkyl group. We detected this C=C absorption in IR transmission spectra on high surface area substrates such as silicon nanowires and porous silicon (fig 4.9.) but never saw it on planar silicon wafers, most likely because of sensitivity reasons. We assume, although it couldn't be confirmed, that the chemistry on this substrate equals the chemistry on high surface area substrates, forming an alkenyl monolayer upon hydrosilylation.



Figure 4.9 Transmission IR spectrum of H-terminated silicon nanowires before (a) and after (b) hydrosilylation with octadecyne.

Other characteristic IR bands observed on those substrates were v(CH₃) at 2960 cm⁻¹, v(CH₂) at 2925, 2856 and δ (CH₂) at 1465 cm⁻¹ all confirming the formation of a hydrocarbon adsorbate. Due to the high surface are of these substrates there is a possibility that physisorption of the alkyne precursor is responsible for some of the CH_x absorption. To minimize the risk of such physisorption, porous silicon was sonicated in ethanol and toluene for 5 min. Further sonication leads to no further intensity changes in the CH_x bands, hence it could be assumed that the CH_x stretching bands correspond to alkyl chains covalently bonded to the substrate through a Si-C bond. Silicon nanowires were cleaved off the substrate upon sonication in ethanol and heated to 50 °C for 60 min to remove any physysisorbed alkyne.

Both porous silicon and silicon nanowires could be characterized with transmission IR and reflection IR. Because of the high surface roughness of both of those substrates, the incident beam is strongly scattered after interacting with the surface, allowing Diffusion Reflection Infrared Fourier Transformation (DRIFT) to be carried out with an optimal angle of incidence of 15°.

Wafers recorded in DRIFT are limited to the size of the sample holder and the spectra are often suffering from baseline shifts and other spectral artefacts. However, DRIFT is the only applicable IR method for longer, ordered nanowires, which become intransparent for IR radiation after an etching time of about 60 min (see Fig. 4.7). However, because nanowires 20 μ m long (etching time of 30 min) have a large enough surface area to obtain a satisfactory

SNR even from submonolayer coverages, IR transmission measurements were usually used to follow the surface modification reactions of Si nanowires. Table 4.3. brings a compilation of experimental results from Ellispometry, Contact Angel and RAIRS measurments for different silicon substrates functionalized with alkyl groups of different chain lengths.

Method	Si-wafer (H)	Si-wafer (C18)	Si-wafer (C15)	Si-wafer (C12)
Ellipsometry	3 Å	21 Å	16 Å	14 Å
WCA	83°	109°	106°	
RAIRS	2085 cm ⁻¹ ,	2920 cm ⁻¹ ,	2920 cm ⁻¹ , 2850	2920 cm ⁻¹ , 2850
	2115 cm ^{-1,}	2850 2963 cm ⁻¹	2963 cm ⁻¹ and	2963 cm ⁻¹ and
	2142 cm-1	and 2872 cm ⁻¹ .	2872 cm ⁻¹ .	2872 cm ⁻¹ .
	PSi (H)	PSi (C18)	SiNW (H)	SiNW (C18)
FTIR	2085 cm ⁻¹ ,	2920 cm ⁻¹ ,	2085 cm ⁻¹ ,	2920 cm ⁻¹ , 2850
	2115 cm ⁻¹ ,	2850 2963 cm ⁻¹	2115 cm ⁻¹ ,	2963 cm ⁻¹ and
	2142 cm-1	and 2872 cm ⁻¹ .	2142 cm-1	2872 cm ⁻¹ . 1600
		1600 cm ⁻¹ ,		cm ⁻¹ , 1400 cm ⁻¹
		1400 cm ⁻¹		
WCA	110-130°	110-130°	160-170°	160-170°

Table 4.3 Characteristics of oxide free Si(100) wafer, porous silicon and silicon nanowire before and after hydrosilylation with octadecyne (C18), pentadecyne (C15) and dodecyne (C12).

4.2.2. Surface orientation of alkyne monolayers on Si (100) wafers

RAIRS was applied to investigate the degree of order and the surface orientation of alkyne monolayers adsorbed on planar silicon. This information can be obtained by measuring the CH stretching vibrations, which are extremely sensitive to the structure of the monolayer. A high degree of structural order was confirmed by the highly anisotropic character of the spectrum exhibiting both positive and negative peaks. The spectrum shows 2 positive CH₂ peaks at 2920 cm⁻¹ (v_{as} (CH₂)) and 2850 cm⁻¹(v_{s} (CH₂)) as well as 2 negative peaks at 2963 cm⁻¹(v_{as} CH₃)), 2872 cm⁻¹ (v_{s} (CH₃)) resembling RAIRS spectra of highly ordered monolayers of alkyltrichlorosilanes on oxidized silicon. The monolayer thickness was determined to 21 A and the water contact angle was determined to 108 +/- 1°, both highly characteristic for an ordered well packed monolayer.

3 different structure models (Fig 4.10) were utilized to calculate spectra which resemble the experimental ones in order to determine the degree of order. In model A the monolayer is perfectly anisotropic with ordered CH₂ and CH₃ groups and with the chain axis tilted by an agle of α or -. α to the surface normal. The sign of the tilt angle has no influence on the surface orientation of the CH₂ groups. The surface orientation of the terminal CH₃ groups, however, is different for positive and negative angles. Using this model, the tilt angle of monolayers of trichlorosilanes could earlier be determined to approximately $10^{\circ 79}$. Model B renders a mixture of a partly isotropic film, with an ordered well defined CH₂ chain but with the methyl groups randomly oriented, were each vibrational dipole assumes the isotropic tilt angle of 54.7° (averaged angle over all possible spatial directions) with respect to the surface normal. In this model the sign of the tilt angle α has no influence on the surface orientation and on the IR absorption intensities any more. The third model is completely isotropic with no structural order, resulting in a uniform isotropic tilt angle for all vibration dipoles.



Figur 4.10. Different structural models of monolayers of octadecyne adsorbed on silicon surfaces. A)Anisotropic model with all-trans hydrocarbon chains. Note that the orientation of the terminal CH3 groups depends in this case on the sign of the tilt angle α . B) Mixed anisotropic/isotropic model with all-trans CH2 groups but randomly oriented CH3 chain terminal. The methyl groups orientation is independent of the value and the sign of the chain tilt angle. C) Isotropic model with randomly oriented molecules

Figure 4.11 shows the experimental monolayer spectrum (A) in the CH stretching region of octadecyne on a Si(100) wafer measured in Reflection Absorption Infrared Spectroscopy

with angle of incidence of 80° together with the calculated spectra (Figure 4.11 B-D) of a hexadecyl group on a silicon surface for the 3 different structural models discussed above: an all-trans geometry (model A) with a chain tilt angle of +31° (Fig 4.11B, solid line) and -31° (Fig 4.11B, broken line), a mixed isotropic/anisotropic structure (model B) with all-trans methylene chains tilted by 31° and disordered methyl groups (Fig 4.11 C) and a completely disordered structure (Fig 4.11 D)



Figur 4.11 Experimental and simulated IR external reflection spectra of a high quality monolayer (d = 2.1 nm) of octadecyne adsorbed on Si (100) (p-polarized light, 81° incidence) a) experimental spectrum b) simulated spectrum for a fully anisotropic monolayer (model A) with a chain tilt angle of + 31° (solid line) and -31° (broken line) c) simulated spectrum for a mixed anisotropic/isotropic monolayer (model B) with a 31° chain tilt angle d) simulated spectrum for a fully isotropic monolayer (model C)

Fig. 4.11c clearly gives the best fit. The tilt angle of 31° resulting from these simulations is in good agreement with previously reported values derived from x-ray reflectivity⁹⁸, ellipsometric film thicknesses⁶⁶ or from dichroic ratios^{66,97–99} in ATR infrared spectra. The error margins of these previous data have been estimated to be fairly high, whereas the infrared external reflection spectra presented here yield an accuracy for the chain tilt angle of a few degrees, as shown in Figure 4.12.



Figur 4.12. A) Experimental octadecyne monolayer layer spectra of five different samples with thicknesses between 1.95 nm and 2.1 nm B) Simulated octadecyne monolayer spectra as in Fig. 4.13 c) (model B) for three different chain tilt angles $\alpha = 28^{\circ}$, 31° and 34° .

Figure 4.12A shows spectra of five independent samples of octadecyne monolayers, which illustrate the reproducibility of the peak intensities in comparison to the predicted spectral changes due to a tilt angle change of $\pm 3^{\circ}$ (Fig 4.12B). Whereas the calculated spectrum for $\alpha = 28^{\circ}$ yields v(CH₂) peaks clearly stronger than in the experimental spectra, the simulated spectrum for $\alpha = 34^{\circ}$ shows v(CH₂) intensities clearly smaller than the experimental spectra. Moreover, the v(CH₂) absorptions for $\alpha = 34^{\circ}$ assume distinct derivative peak shapes, which are caused by the increasing perpendicular component of the v(CH₂) transition dipoles with increasing α , giving rise to negative peaks at slightly higher wavenumbers than the positive, parallel component (an effect known as TO-LO splitting¹⁰⁰). Based on the results shown in Fig. 4.12 the alkyl group tilt angle is determined to 31± 3°.

Although a careful preparation of the monolayer films under rigorous exclusion of oxygen normally yields high quality, ordered monolayers with very good spectral reproducibility (see Figure 4.12A) and film thickness variations of ± 0.1 nm, lower quality films are produced from time to time, presumably due to adventitious surface contaminations and/or partial surface

oxidation. Such lower quality films are often characterized by a slightly smaller film thickness and lower water contact angles, and also show strongly altered IR reflection spectra (Fig. 4.13). In Figure 4.13 A, the spectrum of an octadecyne monolayer with 1.9 nm thickness is shown, displaying strongly derivative-shaped $v(CH_2)$ absorptions and negative $v(CH_3)$ peaks. Although derivative peak shapes are also predicted for an ordered monolayer with a chain tilt angle $> 34^{\circ}$ (see Figure 4.12B), the more likely interpretation of the spectra in Figure 4.13 is a film structure containing ordered and disordered domains. The experimental spectrum was therefore fitted as a mixture of a highly ordered (model B) and a disordered contribution (model C) and yields a very good agreement for a 74% ordered and 26% disordered ratio (Figure 4.13A, broken line). Figure 4.13B shows another example of a more disordered monolayer, where oxygen has been deliberately leaked into the reaction vessel to give a monolayer of clearly diminished quality with a thickness of only 1.6 nm. Although all signs of structural order (positive $v(CH_2)$ peaks) seem to have disappeared in this spectrum, the v(CH₂)/ v(CH₃) peak intensity ratios are considerably smaller than for a completely isotropic film (see Fig. 4.11D) as a consequence of "hidden" positive contributions from ordered film domains. The best fit for this spectrum is obtained for an ordered/disordered percentage of 59:41 (Figure 4B, broken line).



Fig 4.13. Experimental and simulated IR spectra of lower quality monolayers of octadecyne on Si (100). The simulated spectra were calculated as mixtures of ordered (model B) and disordered (model C) domains: a) 74 % ordered b) 59% ordered



Figur 4.14 Experimental and simulated IR spectra of high quality monolayers of a) pentadecyne (d = 1.65 nm) and b) dodecyne (d = 1.5 nm). As in Fig. 1d), a mixed anisotropic/isotropic film structure with a 28° tilt angle of the CH2 skeleton gave the best fit of the experimental spectra.

Fig. 4.14 shows the experimental and simulated IR reflection spectra of monolayers of 1pentadecyne and 1-dodecyne on Si(100). The spectra look qualitatively very similar to the spectra of high-quality octadecyne films and show essentially identical peak maxima. Only the $v(CH_2)$ absorption intensities are reduced due to the smaller number of methylene groups in the film molecules. An essentially identical, highly ordered structure is therefore implied also for these shorter-chain molecules, and the best fits to the spectra are obtained for an assumed 28° tilt angle for both compounds. The success rate of forming high-quality monolayers with these short-chain compounds decreases and the error margins for the chain tilt angle increases slightly to an estimated \pm 5°. Structural disorder is again very clearly indicated by a partial or complete inversion of the $v(CH_2)$ absorptions (spectra not shown).

As described in section 2.3.1., the intensity of an absorption band in a reflection spectrum can be expressed as $-\log R_s/R_0$, where R_s is the sample (substrate plus adsorbate) reflectivity and R_0 is the reflectivity of the clean substrate at the frequency of the absorption maximum .The peak intensity depends, in addition to the orientation of the dipole moment, also strongly on the incidence angle of the infrared beam and on the polarization direction.

For p-polarized light, the band intensities increase with increasing incidence angle while retaining the initial band directions, until a sudden band inversion at the Brewster angle (73° for silicon) occurs. This was observed for OTS monolayers on oxidized silicon wafers where the negative v(CH3) as well as the positive v(CH2) bands changed direction and resulted in identical inverted IR spectra (Fig 4.15a-b). The spectrum of a disordered film of octadecyne adsorbed on oxide free silicon surface was also inverted upon crossing the Brewster angle: Only negative peaks were observed above the Brewster angle (Fig 4.15c) as expected for a

disordered, isotropic film structure and only positive peaks were measured below the Brewster angle (Fig 4.15d). A quite unexpected and not yet explainable result was obtained for ordered films of octadecyne (Fig. 4.15e,f):





Ordered OTS monolayer









Figure 4.15. Experimental RAIRS spectra (solid lines) and calculated spectra (dotted lines) at 80° and 60° incidence angle of(a-b) an ordered OTS monolayer on native silicon, (c-d) a disordered octadecyne monolayer on silicon and (e-f) an ordered octadecyne monolayer on silicon.

The spectrum of ordered octadecyne at 80° incidence (Fig 4.15e) is essentiall identical to the spectrum of OTS (Fig. 4.15a). Whereas all the peaks invert for OTS at 60° incidence (Fig 4.15b), as predicted by theory, only the CH_3 peaks invert for octadecyne and the CH_2 peaks retain their positive direction (Fig 4.15f). The reason for thes discrepancies are yet unknown.

Summary

Monolayers of long-chain, terminal alkynes $C_nH_{2n}+1C\equiv CH$ (n=10, 13, 16) yield highly ordered structures with a uniform chain tilt angle, if prepared under optimized experimental conditions under rigorous exclusion of oxygen. External reflection IR spectroscopy in combination with spectral simulation routines yield tilt angles of $31\pm3^{\circ}$ for octadecyne (n=16) and $28\pm5^{\circ}$ for pentadecyne (n=13) and dodecyne (n=10) monolayers. Lower-quality films with often unchanged ellipsometric film thicknesses yield markedly different IR spectra, which could be identified as due to mixtures of ordered and disordered film domains and allow a quantitative evaluation of the degree of disorder.

In general, monolayers of alkynes on Si(100) surfaces seem to be less ordered than silanes on silica or thiols on gold because the terminal CH_3 groups of alkyne monlayers are randomly oriented in contrast to the othe systems. One possible reason for this could be the surface roughness of about 3 Å of hydrogen terminated Si(100) as opposed to the perfectly flat, oxide-covered Si(100) substrate. Another possible reason is the stability of the Si-C bond (Si-C bond energy 4 eV compared to 0.11 eV⁴⁵ for Au-S bonds of thiols on gold). Although stable monolayers are desirable because of more robustness against oxidation and heat, it is also much harder for such strongly bound molecules to rearrange on the surface and pack into a oriented, highly ordered structure.
4.2.3 Wetting properties of alkyl modified silicon substrates

The influence of surface porosity on wetting properties

Fig 4.16 shows contact angle measurements on a silicon wafer, porous silicon and silicon nanowires, which exhibit interesting trends and differences between these substrates and demonstrate a pronounced influence of the surface porosity and the surface composition (coating) on the wetting properties. The water contact angle on flat hydrogen terminated silicon was determined to slightly above 80°, which is under the critical angle of 90°. This means that structured silicon surfaces following the Wenzel model will exhibit a decrease in water contact angle compared to flat silicon surfaces (see Fig 2.4). This is, however not observed experimentally, instead, the water contact angle increased to 130° on hydrogen terminated porous silicon and further up to 170° on hydrogen terminated silicon nanowires. Thus, silicon nanowires exhibit what is called "superhydrophobic" properties, i.e. water contact angles > 150°. This increase of an initially hydrophilic contact angle < 90° of the flat substrate into the hydrophobic (>90°) or superhydrophobic (>150°) regime can only be explained by a Cassie-Baxter type wetting (see Fig. 2.5), although a transformation from the Cassie-Baxter state to the Wenzel state normally occurs for $\theta < 90^\circ$. Coating the substrates with octadecyne, results in an increase in water contact angle on flat silicon substrate from 80° to 109°. Nanostructured silicon, however, gave essentially the same contact angles for the uncoated (H-terminated) and the octadecyne-coated substrates. This indicates that among the two major factors determining the wetting properties - chemical composition and surface morphology – the latter one is completely dominating in the systems studied here.



Figure 4.16. Illustration of how roughening the surface influences the contact angle on flat silicon, porous silicon and silicon nanowires coated with octadecyne.

In addition to water, the contact angle of ethyleneglycol was also measured on the different substrates (Fig 4.17a). Ethyleneglycol is less polar and the water contact angle on hydrogen terminated flat silicon surfaces was distinctly lower, approximately 60°. Roughening the surfaces resulted, contrary to the water contact angles, in a decrease in water contact angle on porous silicon to less than 40° and full wetting (θ <10°) on silicon nanowires, as predicted by the Wenzel wetting model (Fig 2.4). Thus, Cassie-Baxter wetting for water changes to Wenzel wetting for ethylene glycol on hydrogen-terminated silicon substrates.

On coated flat silicon surfaces the WCA of ethylene glycol increases to 79°. On porous silicon this angle decreases to slightly above 72°, thus still exhibiting Wenzel wetting properties. On silicon nanowires, in comparison, the WCA increases up to 150° in accordance with the Cassie-Baxter model. Thus, it seems that there is some critical contact angle θ_c around 70° on flat surfaces, where the wetting of the corresponding structured substrates changes suddenly from Wenzel-type for $\theta < \theta_c$ to Cassie type for $\theta > \theta_c$.

Fig 4.17b shows the contact angles as a function of the porosity for hydrogen-terminated and octadecyne-coated silicon substrates with water and ethylene glycol. The porosity of flat silicon is 0 and the porosity of silicon nanowires is assumed to be close to 1 as water contact angles over 170°C are measured (see Fig. 2.5). The porosity of porous silicon is assumed to be somewhere around 0.4 and probably varies quite aubstantially from sample to sample as the etching is not completely reproducible.

Porous silicon has a critical angle of slightly less than 80°, where a transition to the Wenzel state occurs and roughening results in $\theta < \theta c$. On silicon nanowires, this critical point is lower, somewhere between 60° and 77° as judged from the increase in ethylene contact angle on the octadecyne-coated substrate and a decrease on the hydrogen-terminated substrate. It can be assumed that the Cassie-Baxter wetting on porous silicon is harder to maintain compared to silicon nanowires with their very small, sharp needle array, having a greater amount of air under the water droplet. Hence porous silicon reaches the critical point, where a transition between the Cassie-Baxter state to the Wenzel state occurs, earlier than a nanowire array.

From the contact angle measurement with water and ethyleneglygol could thereby be confirmed that the hydrosilylation reaction indeed take place on all three substrates. The surface free energy of hydrogen terminated and coated flat silicon were subsequently determined by the method of Owens–Wendt–Rabel-Kaeble (OWRK) confirming a significantly lower surface energy of coated flat silicon substrate, 22 mN/m compared to 48 mN/m on the hydrogen terminated surface.



Figure 4.17 a) Contact angle of water and ethylene glycol on H-terminated and octadecyne-coated silicon substrates. b) *same as a) but drawn as a function of substrate porosity*

4.2.4. Oxidation of bare and alkylated silicon surfaces

Oxidation in ambient atmosphere

The hydrosilylation reaction competes with the much faster surface oxidation, hence for successful attaching of organic monolayers, a strict moisture- and oxide-free environment is demanded. Bare, hydrogen-terminated silicon surfaces are not stable for more than 10-15 minutes in air and form a native oxide layer 10-15 Ångström thick, hence non-reacted Si-H sites of the initial surface will oxidize..



Figure 4.18 Contact angle measurements of H-terminated and octadecyne coated silicon substrates exposed to 60°C in an oven

Contact angle measurements were used to monitor the rate uf surface oxidation on hydrogen-terminated and octadecyne-coated silicon substrates (silicon wafers, porous silicon and silicon nanowires). The polar surface oxide decreases the water contact angle drastically in comparison to a H-terminated or an alkyl-covered surface, and therefore the contact angle is a rather sensitive parameter for the extent of surface oxidation. The results of these

measurements are shown in Fig. 4.18. A temperature of 60°C was chosen in order to accelerate the rather slow oxidation of H-terminated silicon surfaces. It can be seen clearly from Fig. 4.18, that the octadecyne coating provides an excellent protection against surface oxidation for all three types of substrates, whereas the uncoated, H-terminated surfaces oxidize rapidly under the conditions of these experiments.

Oxidation in basic solution

Hydrogen terminated silicon surfaces are quite unstable in aqueous basic solutions¹⁰¹. When exposed to alkaline solutions, they are etched according to the following reaction.

Si + $2H_2O + 2OH^-$ [Si(OH)₂O₂]²⁻ + $2H_2$

Chemical etching initiated by OH⁻ attack is highly anisotropic, however, in contrast to etching in fluoride solutions where electron holes are directed to pore holes favouring etching, etching in alkaline solutions is a thermally activated process and occurs essentially only at step edges. Thereby, initiation by hydroxide attack leads to the production of atomically flat surfaces , which is used in a process called chemically polishing of silicon wafer surfaces. Here, the stability of H-terminated and octadecyne-coated Si nanowires in aqueous NaOH solution of pH 12 was investigated by secondary electron microscopy. Fig. 4.19. shows SEM images of uncoated and coated SiNWs after different immersion times in the basic solution. H-terminated silicon nanowires are completely etched away already after 1 h exposed to NaOH with only some stumps remaining. Those stumps are also etched away after longer exposing times forming a flat surface. However, silicon nanowires coated with an octadecyl monolayer prevail the attack of the hydroxyl group and the nanowires are intact and essentially unchanged even after 12 h exposure.



1 h exposure

Figur 4.19. Stability of coated and uncoated silicon nanowire in alkaline solution (R.T. pH12)

12 h exposure

Summary

Interesting differences in the wetting properties of the H-terminated and alkyl-coated silicon substrates were observed as well as the great influence of the surface roughness on the wetting properties. The critical contact angle where a transition between the Cassie state and the Wenzel state occurs on structured surfaces was found here as low as about 78°. This is an interesting and unexpected result as it is normally believed that a Cassie state can only occur for an intrinsic contact angle (also called $\theta_{\text{ flat}}$) larger than 90°. There are, however, a few reports in the literature dealing with superhydrophobic surfaces with intrinsically hydrophilic properties (θ_{flat} <90°), where the surface consists of micro textures with so-called overhang structures¹⁰². One example of such a surface is the well known superhydrophobic

lotus leave³⁵. On the nanowires prepared in this thesis, however, such a topology was not aimed for and the SEM images show straight, vertical nanowires. Thus the superhydrophobicity observed with these samples cannot be explained by such overhang structures. Another interesting, future aspect of these studies is the construction of superoleophobic surfaces, i.e. surfaces which repel water but also oils and hydrocarbon solvents. Whereas superhydrophobis surfaces are quite common in nature, for example the already mentioned lotus leave, the water strider legs, a special kind of butterflie's wings and other plant leves, there is no natural superoleophobic surface known and also synthetic examples are rare, because it is not clear yet what makes a surface superoleophobic. In light of some very promising applications, e.g. for stain resistant materials or for oil-water separation, one can expect consolidated research efforts in this field in the near future Another interesting result of the studies described in this chapter is the very efficient protection of silicon nanowires against corrosion in alkaline solution. Also this can be expected to be of practical importance for the protection of SiNW based devices like field effect transistors or solar cells.

4.3. Adsorption of activated alkynes

4.3.1. Propiolic acid mono- and diesters

Liu et. al¹⁰³ recently presented a mild and efficient Si (111) surface modification procedure via hydrosilylation of activated alkynes such as propiolate esters, propiolic acid, but-3-yne-2-one, propiolnitrile and phenylacetylene. The very mild reaction conditions inspired us to investigate this approach further on flat silicon, porous silicon and silicon nanowires.

The silicon substrates were modified with 3 different terminal propiolate esters, a longchain monoester (tetradecanolpropiolate, TDP), a longchain diester (decadioldipropiolate, DDDP) and a short chain diester (ethanediol dipropiolate, EDDP). Si(100) wafers were first exposed to neat DDDP under Ar atm at 170°C. However, DDDP was fully polymerized to a solid polymer under these conditions, precluding this condition for monolayer adsorption. To avoid polymerization, the esters were therefore adsorbed in solution (0.2 M in mesitylene) at lower temperatures.



Figure 4.20. RAIRS spectra of tetradecanolpropiolate (solid line) and pentadecyne (dotted line) adsorbed on a Si(100) wafer

Tetradecanolpropiolate was attached via hydrosilylation to a Si(100) wafer surface under relatively mild condition (120 °C, 15 h). The RAIRS spectrum shown in Fig. 4.20 resembles the spectrum of a pentadecyne monolayer with 2 positive CH₂ peaks at 2920 cm⁻¹ (v_{as} (CH₂)) and 2850 cm⁻¹(v_{s} (CH₂)) as well as 2 negative peaks at 2963 cm⁻¹(v_{as} CH₃)) and 2872 cm⁻¹ (v_{s} (CH₃)). The monolayer formed from the activated alkyne clearly has an ordered structure similar to adsorbed n-alkynes as judged from the anisotropic character (positive and negative peaks) of the RAIRS spectrum. The weaker peak intensities and the slightly distorted peak shapes, however, indicate a slightly lower surface coverage and a partly disordered film structure compared to n-alkyne monolayers. This might be due to steric reasons caused by

the bulky terminal ester group. The different adsorption conditions (0.2 M solution at 120° instead of neat alkyne at 170°) might further hamper the formation of a perfect ordered monolayer,Other characteristic IR vibrations such as the C=O stretching at 1700 cm-1 and the C=C absorption at 1600 cm⁻¹ couldn't be detected, presumably because of insufficient sensitivity.

Subsequently, the 2 diesters DDDP and EDDP were in the same manner adsorbed onto a Si(100) wafer. Their shorter chain lengths and diminished peak intensities, however, precluded a characterization with RAIRS. A different, more sensitive IR technique attenuated total relfection (ATR) - was therefore employed. The ATR spectra of TDP, DDDP and EDDP are shown in Fig 4.21b and evidence the successful adsorption of all 3 compounds on the polycrystalline Si surface of the ATR element. The TDP spectrum shows the CH₂ peaks at 2925 cm⁻¹ (v_{as} (CH₂)) and 2855 cm⁻¹(v_{s} (CH₂)) as well as a peak at 2963 cm⁻¹ ¹ ($v_{as}CH_3$)). The wavenumbers are slightly shifted compared to TDP adsorbed on a Si(100) wafer, which indicate a less ordered monolayer film. One possible reason for these differences might be the significantly larger amount of solvent necessary for the adsorption, on the ATR crystal (20 mL compared to 3 mL), which might introduce additional oxygen and contaminate the surface. The C=O stretching region in the ATR spectra of Fig. 4.21b is, unfortunately, shadowed by a strong intrinsic absorption of the ATR crystal and does therefore not allow any conclusive band assignments in this region. The ATR spectra of DDDP and EDDP in Fig. 4.21b show in addition to the $v(CH_2)$ absorptions the $v(C\equiv C)$ stretching band at 2121 cm⁻¹ of the terminal alkyne group. The terminal v(H-C) absorption, which is expected around 3260 cm⁻¹, is not detected, presumably due to lack of sensitivity.

The mono- and dipropiolate esters were further adsorbed onto porous silicon and on silicon nanowires to achieve information on how the surface morphology influences the adsorption Transmission FTIR measurements of TDP adsorbed on silicon nanowires clearly evidenced a successful adsorption (Fig 4.21a). In addition to the CH₂ and CH₃ absorptions that could be detected also on Si(100) wafers, the ester v(C=O) peak at 1726 cm⁻¹. and the CH₂ deformation mode at 1451 cm⁻¹ were assigned. Also, successful adsorption of the diesters DDDP and EDDP on Si nanowires could be derived from the IR spectra in Fig 4.21a, which show absorptions of the terminal alkyne groups of adsorbed DDDP and EDDP at 3263 cm⁻¹ (v(H-C)) and 2121 cm⁻¹ (v(C=C)) as well as the ester v(C=O) peak at 1726 cm⁻¹. The CH₂ absorptions appear below 3000 cm⁻¹ and the CH₂ deformation mode at 1451 cm⁻¹ where A(C=O) is the integral of the C=O peak and A(CnH_{2n}/n) is the integral of the CH stretching peak divided by the number of carbon atoms, is approximately twice as large for DDDP (4.8) compared to TDP(2.3) as expected due to the second carbonyl group of the diester.



Figure 4.21 IR spectra of different silicon substrates modified with TDP, DDDP and EDDP a) silicon nanowires b) flat polycrystalline silicon (ATR crystal) c) and porous silicon.

IR spectra of the propiolate esters adsorbed on porous silicon are shown in Fig 4.21c. The spectrum of adsorbed TDP resembles the spectrum of TDP on nanowires with a ratio $A(C=O)/A(C_nH_{2n}/n)$ of 2.6. The DDDP and EDDP spectra on porous silicon differ, however, clearly from the other substrates and do not show the characteristic alkyne peaks at 3263 cm⁻¹ (v(H-C)) and 2121 cm⁻¹ (v(C=C)). The latter would also be hard to detect because of strong Si-H stretchings in this region. The C=O peaks is present at 1725 cm-1 and the (C=O)/A(C_nH_{n-1}/n) is 4.8, i.e. again – as on Si nanowires - approximately twice as large as adsorbed TDP, indicating that the diesters were successfully attached onto porous silicon surfaces although the terminal alkyne group could be detected in the IR spectra. A possible explanation could be that that the inhomogeneous morphology and concave surface geometry of porous silicon enables the diynes to bind with both terminal alkyne groups to the substrate. This is illustrated in Fig. 4.26 and will be discussed in more detail later.

4.3.2. Reversible acid-base surface reactions of adsorbed propiolic acid.

Recently Imanishi et.al¹⁰⁴ reported on reversible acid-base surface reactions on oxide free Si(111) surfaces modified with α,β -unsaturated carbonyl compounds via hydrosilylation, As electron deficient alkynes are more reactive and allow the hydrosilylation reaction to be carried out under more moderate conditions, propiolic acid or acrylic acid and its derivatives are interesting precursors to functionalize silicon surfaces under mild conditions. By treating the carboxylic acid terminated surface alternatively with acid and alkaline solution, it was possible to reversibly transform this functionality between the acid and the acid salt. Transfer between the acid and the salt of the adsorbed film will potentially change the electronic properties (e.g. the conductance) of the silicon substrate and, hence allowing it to be as a simple sensor or switch. This study inspired us to try this approach for the functionalization of Si nanowires and porous Si. Figure 4.22 a) shows the resultant transmission spectrum of H-terminated porous silicon exposed to a 0.5 M propiolic acid/mesitylene solution for 12h at 120 °C. The peak at 1719 cm-1 is assigned to the C=O vibration of the COOH group confirming that propiolic acid was attached to the Si surface, mainly in its acid form, however a weak band at 1560 cm-1 indicated that a minor part was ionized..



Figure 4.22 IR transmission spectra of porous silicon coated with propiolic acid a) spectrum of a freshly coated substrate b) after rinsing in 0.01 NaOH solution. c) after further rinsing in 2.0 M HCl solution.

The small peak at 1605 cm⁻¹ assigned to the C=C bond indicates that propiolic acid is attached to the Si surface via hydrosilylation of the alkyne group and not through a side reaction of the carboxylic group. The spectrum of the Si surface after rinsing in 0.01M NaOH solution is shown in Figure 4.22b. The major absorption appears at 1575 cm-1 and is assigned to the $v(COO^{-})$ stretching vibration of the carboxylate group, indicating that the carboxyl group is ionized to its corresponding salt in alkaline solution. Exposing the alkalitreated substrate to 2.0 M HCl solution results in the disappearance of the 1575 cm-1 salt and regeneration of the original 1719 cm⁻¹ absorption of the undissociated carboxylic acid.

A monolayer of propiolic acid adsorbed on porous silicon therefore allows reversible switching between the acid and the basic form of the surface acid groups.

Propiolic acid functionalized porous silicon substrates were subsequently placed in an oven heated to 170 °C in order to explore the thermal stability of the acid monolayer. Fig 4.23. shows the IR spectra monitoring potential thermally induced damage to the monolayer.



Figure 4.23 IR spectra of propiolic acid adsorbed on porous silicon and annealed at 170°C for different times. a) freshly adsorbed propiolic acid b) after 5 min at 170 °C c) after 30 min at 170 °C d) after 16h at 170 °C e) after 7 days at 170 °C f) after subsequent exposure to 0.01 M NaOH g) after subsequent exposure to 2M HCl

Exposing the substrate for 7 days did not result in any decrease in the intensity of the acid carbonyl peak.. However, the peak maximum shifted from 1719 cm-1 continuously to 1735 cm-1 after one week exposure, whereby a shift of 6 cm⁻¹ was already observed after 5 minutes at 170°C. Subsequent rinsing with 0.01 M NaOH generated a carboxylate salt peak v(COO) at 1576 cm-1 and further rinsing with 2M HCl regenerated the 1725 cm⁻¹ acid peak in complete analogy to the freshly adsorbed, not heated samples. This shows that the chemical properties of this propiolic acid monolayer are unchanged even after one week at 170°. It also demonstrates the very high chemical and thermal stability of these Si-C bonded monolayers. The high wavenumber shift of the C=O peak with increasing high temperature exposure might be explained by an initial H-bonded structure of the freshly prepared sample, which is successively destroyed at higher temperatures, shifting the C=O peak maximum to higher wavenumbers.

Propiolic acid were subsequently adsorbed on silicon nanowire transistors. The idea was that the electron withdrawing oxygen of the carboxylic group will through charge transfer influence the conductivity of the silicon nanowire in a similar way as conventional doping. Attaching a carboxylic acid would potentially allow tuning the electric properties of the silicon nanowire with the pH level.

For this purpose, silicon nanowire transistors were fabricated, containing two Ni contact connected with a Si nanowire allowing the Si nanowire conductance to be measured. The transistors were treated according to the modification procedure described, oxide etching in 5% HF followed by hydrosilylation 0.5 M propiolic acid in mesitylene at 120 °C and the electric properties were subsequently measured. Unfortunately modified nanowires did not conduct any current and the reason for this was clear after comparing SEM pictured of the



Figure 4.24. Silicon nanowire transistors before and after treatment with 5% HF

transistors before and after the functionalization, Fig. 4.24a shows two nickel contacts connected with a silicon nanowire and fig 4.23b shows the same transistors after being treated with 5% HF. The Ni-Silicide contacts are clearly etched away precluding conductance measurements. In order to avoid such as etching, the Ni-Silicide might be protected with a PMMA photo-coating prior to the modification, alternatively the nanowires could be functionalized prior to the fabrication of the transistor.

4.4. Surface functionalization via click chemistry

4.4.1. Copper-catalysed Huisgen cycloadditions

Adding functional groups to the silicon surface is of major importance for practical applications, as mentioned before. This can be carried out in one step, by hydrosilylation with an alkyne carrying the desired terminal functionality, as described in the previous section. However, attaching complex molecules in one step has several drawbacks. One is the time and potential difficulties involved in synthesising the molecule, more important, however, is the often encountered incompatibility between the desired functionalities and the attachment procedure. The desired functionalities must be robust enough to survive the rather harsh reaction conditions of hydrosilylation, such as high temperatures up to 170°C or UV irradiation. Moreover, the desired functionalities may react with the silicon hydride surface which has a broad reactivity spectrum and, besides the hydrosilylation reaction with unsaturated hydrocarbons, has been reported to react with halogens, nitriles, alcohols, aldehydes, and ketones⁵². Hence, it is often a better strategy to immobilize the functionalities onto silicon surfaces in a two-step attachment procedure where a primer layer containing a compatible reactive terminal functionality is covalently attached to the surface and the desired functionality is then added in a subsequent coupling reaction with the primer layer.

One of the most versatile and reliable coupling reactions for this purpose is the copper catalysed Huisgen cycloaddition between an azide and an alkyne, forming a triazole ring in often quantitative yields without any side products. This reaction has proven its versatility and efficiency for surface modifications of a broad range of solid substrates, including oxide-free silicon^{83,85,105–107} and is compatible with a wide range of functionalities. In order to test how the surface morphology affects this modification strategy, this reaction was applied using porous silicon and Si nanowires as substrates.

As described in the experimental section, porous silicon and silicon nanowire substrates were modified with an acetylene terminated monolayer (1,8 nonadiyne), which was subsequently coupled via a Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition reaction (click reaction) with an organic azide R-N₃ The course of this surface click reaction was followed in the infrared spectra (Fig. 4.25) and yielded some pronounced differences between porous Si and Si nanowires as the substrate. The major absorptions in the spectra of the nonadiyne primer layer shown in Fig. 4.25 are the CH₂ stretching absorptions at 2860 and 2930 cm⁻¹ and the terminal v(H-C=C) band at 3322 cm⁻¹. Upon coupling, the v(H-C=C) band is strongly reduced or disappears completely, the v(CH₂) bands increase and an additional

shoulder at 2960 cm⁻¹ assigned to $v(CH_3)$ of the coupled octyl group appears. The peak intensity ratio $v(H-C\equiv C)/v(CH_2)$ in the nonadiyne monolayer spectra was about half on porous silicon (0,08+/-0,03) compared to silicon nanowires (0.16 +/- 0,03), indicating a substantially reduced surface concentration of free, terminal alkyne groups on porous silicon. Moreover, the acetylene-terminated silicon nanowire surface couples quantitatively with azidooctane as judged from the complete disappearance of the $v(H-C\equiv C)$ absorption at 3323 cm⁻¹, whereas a residual $v(H-C\equiv C)$ is seen from unreacted nonadiyne in the spectrum on porous silicon after coupling. Accordingly, the the intensity gain of the $v(CH_2)$ absorptions upon coupling is also much smaller – slightly less than half – on porous Si compared to Si nanowires. The overall surface concentration of coupled azide is therefore estimated to be less than 50% on porous Si compared to Si NWs.





Figure 4.25. IR spectra monitoring the copper catalysed click reaction between 1,8 nonadiyne coated porous silicon (dashed line) and silicon nanowires (solid line) and 1-azidooctan

Similar results of a substantially reduced surface alkyne concentration on porous silicon compared to Si NWs were obtained with the propiolic acid dieseters DDDP and EDDP (section 4.3.1) We therefore postulate here again that the inhomogeneous morphology and concave surface geometry of porous silicon might enable divers to bind with both terminal alkyne groups to the substrate, as shown schematically in Fig 4.26, rendering these molecules unreactive in the subsequent click coupling step. This interpretation is also

supported by a substantially higher $v(C=C)/v(CH_2)$ ratio in the nonadiyne monolayer spectra on porous silicon compared to silicon nanowires (v(C=C)) is the absorption around 1600 cm⁻¹ due to surface-bound alkenyl groups. Moreover, some of the surface alkyne groups might be inaccessible to the azide due to steric reasons, resulting altogether in a strongly reduced reaction yield on porous silicon.



Figure 4.26. Schematic illustration nonadiyne adsorbed on porous silicon and silicon nanowires. The inhomogeneous morphology and concave surface geometry of porous silicon enable diynes to bind with both terminal alkyne groups to the substrate

4.3.2 Copper-free click reactions

Although the copper-catalysed Huisgen cycloaddition is an easy and reliable way to postfunctionalize silicon surfaces with desired groups, the use of copper is a major obstacle and might cause problems in various applications. Traces of copper are known to retain on the surface despite copious rinsing in EDTA and thereby alter the electronic properties of the substrate dramatically¹⁰⁸. In biological environments copper is often precluded because of its cytotoxic properties¹⁰⁹. Copper is also known to cause degradation of DNA molecules¹¹⁰ and to induce protein denaturation¹¹¹.

One alternative solution to bypass the problem caused by copper would be to design a surface with terminal electron deficient alkynes, formed by adding an electron withdrawing group on the gamma carbon atom. Such electron deficient alkynes are known to react with azides in the absence of copper, whereby the surface is turned into a clickable platform, which can, without any additives, be coupled with an over layer of an organic azide carrying the desired terminal functionality. Although such a metal free postfunctionalization strategy of surfaces would obviously be highly preferable, this topic is to date still rather unexplored. This motivated us to explore this approach, aiming a reliable, robust functionalization procedure that allows attachment of functional groups onto oxide-free silicon surfaces under mild conditions without the addition of a metal catalyst

SiNWs about 20 µm long and 80 nm thick were prepared as previously described and subjected to the following surface modification procedure shown schematically in Fig. 4.27: In the first step, the native oxide layer is removed by HF, forming a hydrogen-terminated surface. The next step is a hydrosilylation reaction forming a clickable anchor layer. To form this anchor layer we chose 1,2-ethanediol dipropiolate (EDDP). It is a short chain, activated dialkyne, easy to synthesize and, as shown in chapter 4.3, can be successfully attached to silicon nanowires. The electron withdrawing carbonyl groups are known to activate the terminal alkyne groups, which brings two important advantages for the purpose of this study: First, such activated alkynes are more reactive for hydrosilylation¹⁰³ such that the primer layer formation can be carried out under milder reaction conditions. Second, the subsequent surface click coupling via cycloaddition of an azide can be carried out without copper catalysis. Thus, in summary, this compound EDDP is a promising precursor for the functionalization of silicon surfaces under mild and catalyst-free conditions. The last step of this modification procedure was then the click coupling of the EDDP primer layer with octylazide, which was carried out in by immersion of the EDDP-primed SiNW substrate in a 0.5 M solution for 6 h in ethanol (toluene or DMSO can also be used as solvents alternatively).



Figure 4.27. Water contact angles and infrared spectra of surface-modified silicon nanowires:(a) hydrogenterminated SiNW, (b) after hydrosilylation of (a) with 1,2-ethanediol dipropiolate, and (c) after click reaction of (b) with 1-azidooctane. The course of this surface modification process was followed with infrared spectroscopy. Starting with a H-terminated Si surface (Figure 4.27a) with its characteristic $-SiH_x$ (x = 1, 2, 3) stretching vibrations at 2142 cm⁻¹ (SiH₃), 2110 cm⁻¹ (SiH₂) and 2087 cm⁻¹ (SiH) , these bands disappear completely upon adsorption of EDDP (Figure 4.27b) and are replaced by absorptions of the terminal alkyne groups of adsorbed EDDP at 3263 cm⁻¹ (v(H-C)) and 2121 cm⁻¹ (v(C=C)) as well as the ester v(C=O) peak at 1726 cm⁻¹. The alkyne (v(H-C)) absorption is unusually broad and is shifted by almost 50 cm⁻¹ to lower wavenumbers compared to adsorbed 1,8 nonadiyne. The CH stretching absorptions of EDDP appear below 3000 cm⁻¹ and the CH₂ deformation mode at 1451 cm⁻¹. Clicking 1-azidooctane onto this EDDP monolayer (Fig 4.27c) results in the disappearance of the alkyne v(H-C) and v(C=C) peaks and the growth of the v(CH) and δ (CH₂) absorptions of the octyl group at 2960cm⁻ $^{1}(v_{as}(CH_{3}))$, 2930 cm⁻¹ ($v_{as}(CH_{2})$), 2859 cm⁻¹ ($v_{s}(CH_{2})$) and 1455 cm⁻¹ ($\delta(CH_{2})$). A small peak at 3142 cm⁻¹ is presumably the v(H-C=C) stretching absorption of the single CH group in the triazole ring. The v(C=O) absorption shifts from 1726 cm⁻¹ to 1734 cm⁻¹ upon click coupling. This high frequency shift, together with the broad, low-frequency absorption of v(H-C=C) of adsorbed EDDP in Fig 4.27b, indicates a hydrogen bonding interaction between the alkyne hydrogen and the ester carbonyl group in the EDDP layer, which weakens both the alkyne H-C bond and carbonyl bond and causes a low frequency shift of their stretching absorptions. The click reaction removes the alkyne hydrogen and v(C=O) shifts back to higher wavenumbers in the click product (Figure 4.27c). A blind experiment – exposure of the EDDP monolayer to pure solvent under the same conditions as in the click reaction - vielded an unchanged EDDP monolayer spectrum. Under the current reaction conditions (6h exposure at 50°C), the yield of the surface click reaction is essentially quantitative as judged from the complete disappearance of the terminal alkyne absorptions. Another indication of successful surface modification could also be achieved by following the changes in wetting properties in course of this modification. H-terminated silicon nanowire surfaces have the superhydrophobic wetting properties as a consequence of both structural and chemical factors (see section 4.2.3) with water contact angels of 150-170° depending on the surface morphology. Adsorbing the highly polar EDDP changes the chemical properties and results in a superhydrophilic surface with a water contact angle less than 10°, which upon coupling with azidooctane rises again to about 115°. This latter result is interesting in the sense that densely packed hydrocarbon monolayers on SiNWs have been shown to yield superhydrophobic properties with WCAs of 170° (see. 4.2.3). After click coupling here, the SiNWs should also be covered by a hydrocarbon layer albeit with a somewhat shorter chain length (octyl) than the octadecyne monolayers described in 4.2.3. The measured contact angle of 115° suggests that the octyl layer after click coupling is not as perfect and densely packed as the octadecyl layer adsorbed directly. This is further supported by results for an

incomplete click coupling reaction with only 2h reaction time at 50°C, after which a WCA of only 90° was measured.



Figure 4.28. Click reaction of activated and non-activated alkynes adsorbed on Si nanowires with 1-azidooctane

No reaction occurred when the non-activated 1,8-nonadiyne was adsorbed and exposed under the same reaction conditions to the click reagent 1-azidooctane (Fig. 4.28). Only in the presence of a Cu-catalyst, this latter reaction proceeded quantitatively as shown in Fig. 4.28 and described in more detail in the previous chapter. This proves the importance of an electron withdrawing group at the γ -carbon for successful cycloadditions to be carried out under moderate conditions.

The modification protocol described above was used to attach different functional groups to the silicon nanowires such as phenyl, nitrile and azide (Fig.4.29) . Coupling 1.2-diazidoethane onto the EDDP anchor layers, for example, forms a new clickable platform of an azide terminated surface allowing a second cycloaddition with a terminated alkyne - a so called tandem click reaction - to be carried out. The coupling reactions shown in Fig. 4.29 were equally successful carried out in ethanol, toluene, THF and DMSO, showing that this reaction can be carried out in polar as well as nonpolar solvents. This is another great advantage of this copper-free modification strategy compared to the copper catalyzed version, which, according to previous studies, gave rather poor yields in nonpolar solvents because of insufficient solubility of the Cu catalyst¹¹². To be able to carry out the coupling in nonpolar solvents is obviously a great advantage when attaching large nonpolar molecules

like long-chain hydrocarbon compounds, which are insoluble in the standard $H_2O/EtOH$ solution commonly utilized for the copper catalysed click reaction. Moreover, the silicon substrate may be more resistant to oxidation in nonpolar solvents compared to polar solvents because of their generally lower O_2 solubilities.



Figure 4.29. Surface click coupling of different target functionalities onto silicon nanowires primed with ethandiol dipropiolate (EDDP)

The surface modification procedure was also successfully carried out on planar Si. Due to the limited sensitivity of RAIRS, the modification was followed by ATR as shown in Fig 4.30. The surface in this case is a polycristalline silicon surface and certain spectral differences in band shapes and peak positions compared to Si(100) as a substrate must be ascribed to the different surface crystal structure. Starting with the hydrogen-terminated surface yielding a broad band at 2100 cm-1-2190 cm-1(Fig. 4.30, upper spectrum), the SiH_x band disappears as on silicon nanowires upon adsorption of EDDP and is replaced by a sharp v(C=C) stretching absorption at 2120 cm-1 (Fig. 4.30, middle spectrum), which upon exposure to 1-azidooctane at 50 °C completely vanishes.(Fig. 4.30, lower spectrum). As the ATR crystal absorbs radiation slightly above 1700 cm-1, an analysis of the C=O stretching absorption was prohibited. The triazole absorption at 3142 and the v(C=C) stretching band around 1600 cm⁻¹ could not be detected, presumably because of insufficient sensitivity.



Figur 4.30. Infrared spectra of surface-modified silicon ATR crystals. Top: a hydrogen-terminated ATR crystal. Middle: after hydrosilylation with 1,2-ethanediol dipropiolate Bottom: after click reaction of with 1-azidooctane.

As mentioned in chapter 4.3, EDDP adsorbed on porous silicon yielded a different spectrum than with silicon nanowires or Si wafers. It did not exhibit the peak at 2120 cm-1 nor the peak at 3300 cm⁻¹, neither was an increase in the CH stretching absorptions observed after cycloaddition. The C=O, C=C and CH absorptions were detected, however, indicating that the dialkyne bonds with both alkyne groups to the substrate isimilar to nonadiyne, which essentially prohibited further functionalization.

To prevent such backbonding, an α-alkyne carrying a terminal propiolate group protected with a trimethylsilyl group (hept-6-ynyl 3-(trimethylsilyl)propiolate) was used instead and adsorbed first on a SiNW substrate. The adsorption was successful, as shown by the IR spectrum in Fig 4.31a, however, the removal of the protecting group turned out to be problematic. Deprotection with TBAF in THF, which is a standard, reliable method in solution phase, failed and caused damage to the monolayer resulting in a decreased carbonyl absorption. TBAF has previously been reported to deprotect TMS-groups on monolayers formed by electrografting of diazonium salts¹¹³. Cai et. al.¹¹⁴, on the contrary, who adsorbed long chain alkenes with a terminal protected alkyne group on Si(100) surfaces with the purpose of further functionalization through copper catalysed click chemistry, failed to remove the TMS protecting group in fluoride solutions. They changed the protecting group to GeMe₃, which was successfully removed with copper allowing the deprotection and click reaction to be carried out in one single step¹⁰⁵. Due to our copper free modification approach this solution wasn't an alternative for us. Instead, deprotection in K₂CO₃-saturated EtOH solution was carried out resulting in a partly removal of the TMS protection groups judged from the decrease of the v(Si-C) stretching bands in Fig. 4.31b. However, deprotection was



Figure 4.31. IR spectra of (hept-6-ynyl 3-(trimethylsilyl)propiolate adsorbed on silicon nanowires. a) Freshly adsorbed b)after 1 min deprotection in ethanol saturated with K_2CO_3 . c) after 5 min deprotection c) After 10 min deprotection d) After 20 min deprotection.

not quantitative and with time damages on the monolayer occurred also here, resulting in a decrease in the v(C=O), $v(H-C\equiv C)$ and $v(CH_x)$ bands (Fig. 4.31 c-e). This damage on the monolayer is most likely caused by ester hydrolysis, removing the TMS protected propiolate group altogether under forming an alcohol-terminated surface. Hence the modification strategy described in this chapter is primarily suitable to silicon nanowires and to flat silicon surfaces, whereas some improvements stil have to be found for porous silicon substrates.

Regioselectivity of metal free click chemistry

Two possible products, the 1,4 isomer and the 1,5 isomer, can be formed in the cycloaddition of an alkyne and an azide. For regioselective formation of the 1.5 product ruthenium catalysts are¹¹⁵ used, whereas copper will direct the coupling to form exclusively the 1.4 isomer¹¹⁶.



One drawback of copper-free click coupling is the loss of regioselectivity. Thermally activated coupling – the major activation used in this work - often tends to produce an isomeric mixture of both the 1.4 and the 1.5 regioisomers. For most applications today, the lack of regioselectivity is not a major concern. However, to design complex surfaces for future molecular nano devices, perfect control of the surface reactions including the substitution pattern of the film molecules, might be required.

Earlier studies on solution phase copper-free azide-alkyne coupling of methylpropiolate (closely related to EDDP), have shown a high percentage of regioselectivity in the coupling with various azides. The ratios 1,4-:1,5 product were consistently about 9:1 in favour of the 1.4 isomer^{117,118}. Based on this study, EDDP was also expected to couple fairly regioselectively with azides and hence keeping a good control on the surface reaction.

Coupling of EDDP with 1-azidooctane in ethanol solution indeed yielded exclusively the 1.4 regioisomer as judged from the single triazole peak in the ¹H NMR and ¹³C-NMR spectra (see experimental section).

This is no guarantee that this regioselectivity is also maintained in a surface reaction. However, because of steric reasons, the regioselectivity is rather expected to increase than decrease in a well packed monolayer on a surface. Such effects of increasing regioselectivity on surfaces compared to solution phase coupling has previously been observed on azide terminated gold nanoparticles, which were coupled with methyl propyonate^{119,120}. The 1,4 isomer was formed exclusively on the gold nanoparticles, whereas the coupling in solution yielded a significant amount of the 1,5 isomer.

Hence there are strong reasons to believe that the coupling of EDDP on silicon surfaces is regioselective, forming mainly the 1.4 regioisomer. However, for applications demanding full control of the surface orientation and stereochemistry, further investigations and experimental evidence are required.

Summary

Two different two-step approaches to modify silicon surfaces with specific functional groups were investigated in this chapter. In the first approach, an alkyne terminated surface was formed through hydrosilylation of an α, ω dialkyne followed by Huisgen copper catalysed cycloaddition between the alkyne terminated surface and an azide carrying the desired functionality. A second, new copper free approach was described where the surface is modified with a terminal electron deficient alkyne which allowed regioselective coupling with azides at 50°C. The absence of copper makes this latter approach compatible with semiconductor technology and it could possibly be applied in the future for a wealth of surface-functionalized devices including catalysts, sensors and electronic devices.

Common to both approaches is that the success of the modification is strongly dependant on the surface morphology of the substrate. Hence, to optimize the surface modifications many aspects must be taken into account, e.g. how shall the molecules be grafted to the surface? is a pre-adsorption approach or a 2 step approach best suited? And how will the surface morphology influence the surface modification procedure

5. Conclusion and Perspectives

It has been demonstrated in this thesis that silicon substrates with different topographies (silicon wafers, porous silicon, silicon nanowires) can be relatively easy prepared and subsequently functionalized with organic monolayers directly bonded to the substrate through hydrosilylation reactions and carrying specific terminal groups located at the monolayer/ambient interface. Their surface chemistry and their structures can be assessed using methods such as FTIR, ellipsometry and contact angle measurements which evidenced some pronounced differences attributed to the different substrate morphologies. FTIR measurements supported by spectra simulations provided detailed information about the molecular orientation and structure of long-chain, terminal alkynes $C_nH_{2n+1}C=CH$ (n=10, 13, 16). The molecule's tilt angle of ordered, long-chain alkyne monolayers on the surface was determined as $31\pm3^{\circ}$ and the structure as a partly isotropic film with an ordered well defined CH_2 chain but with the methyl groups randomly oriented. These results demonstrate again the power of FTIR in determining the chemical composition and structure of monolayer films.

The wetting properties of the substrates were investigated by contact angle measurements and apart from confirming that the hydrosilylation reaction had taken place and that the monolayer protects the surface from oxidation, interesting wetting profiles of the different substrates were achieved, which provided some new, fundamental information about the relative influence of chemical composition and surface morphology on the wettability of surfaces. One particularily interesting and novel result was that the moderately hydrophilic surface of a H-terminated silicon wafer with a water contact angle of 80° turned into a superhydrophobic surface. It is expected that these superhydrophobic properties can be extended to superoleophobic properties, i.e. to be able to fabricate surfaces that repel not just water, but also organic substances. Self-cleaning materials would be only one out of many promising applications of such synthetic surfaces.

The last part of this work was devoted to different approaches for the preparation of surfacefunctionalized monolayers on silicon. Direct, one-step absorption of propiolic acid on porous silicon resulted in a pH-sensitive surface that can be switched between an acidic and a basic form and presents an interesting model system for a pH sensor. Two-step approaches including the popular copper-catalyzed Huisgen cycloaddition and a novel copper-free alkyne-azide cycloaddition were both successfully employed on silicon wafers and silicon nanowires, but failed on porous silicon, likely because the α, ω -dialkyne attached as the primer layer in the first step is double bonded to the substrate, eliminating the second alkyne group for a subsequent cycloaddition. Thus, for a successful surface modification strategy, the substrate's morphology is equally important as the chemical somposition of the surface.

Future work

Silicon has been studied intensively over the past 50 years and - with always increasing demands for miniaturization and improvements in integrated circuit design - this will continue in the near future. Si-C bonded monolayers have been investigated since 1993 when they were first reported by Chidsey and co workers⁹⁹. However, it is still an immature topic and not at all that well explored as, for example, silane monolayers on silicon oxide. Self-assembled monolayers are very important for developing biosensing interfaces, biomimicking surfaces or immobilizing catalysts onto solid supports, because they allow close to molecular level control over the interface design. Hence, strategies to form Si-C bonded monolayers will continue to be developed in the future in order to achieve high quality monolayers under mild conditions and allowing desired chemical functionalities to be introduced with good control on a molecular level. Zhong et. al.⁶⁰ very recently presented room temperature hydrosilylation of alkenes through sonochemical activation and Liu et. al.¹⁰³ presented room temperature monolayer formation with activated alkynes. This indicates that there are still many untried approaches and many parameters to play with in order to achieve a perfect monolayer with a tailored structure and composition under the mildest possible conditions.

In addition, new two-step approaches should be developed and optimized in order to enlarge the pool of functional groups that can be attached to a surface, because many coupling step have previously turned out as relatively inefficient with yields of only 50% or less^{32,121,122}. An exception is the copper-catalysed Huisgen cycloaddition, which proceeds nearly quantitatively on many substrates but has the limitation of requiring a catalyst that is incompatible with electronic or biological applications. Hence we expect that the copper-catalysed click reaction, to date one of the most common ways to functionalize monolayers, will be replaced by copper-free strategies. Such copper-free approaches could be azide-

alkyne coupling with electron-deficient alkynes that until now has caught surprisingly little attention.

The combination of chemical modification and nanostructuring of surfaces are further expected to result in novel materials. Modified silicon nanowire transistors may generate efficient label free sensor devices, monolayers on silicon nanowires may provide a tool to protect silicon from oxidation and tune its electronic properties via charge transfer between surface functional groups and the bulk. Nanostructured silicon has for a long time been expected to revolutionize the world with groundbreaking applications, however, the step from research to real world applications has not been as easy as initially anticipated. The improvements in preparing surfaces with complex, tailored morphologies together with new strategies for chemical modification of those surfaces are very promising and will hopefully bring surface-functionalized silicon into our everyday life sometime soon. To conclude, I believe there are unlimited opportunities in preparing and functionalizing silicon surfaces and we are most likely still at the beginning of this endeavour.

6. References

1. Ciampi S, Harper JB, Gooding JJ. Wet chemical routes to the assembly of organic monolayers on silicon surfaces via the formation of Si–C bonds: surface preparation, passivation and functionalization. *Chemical Society Reviews*. **2010**, 39, 2158.

2. Stewart MP, Buriak JM. New Approaches Toward the Formation of Silicon—Carbon Bonds on Porous Silicon. *ChemInform.* **2002**, 33, 257–257.

3. Shirahata N, Hozumi A, Yonezawa T. Monolayer-derivative functionalization of non-oxidized silicon surfaces. *Chem. Record.* **2005**, 5, 145–159.

4. Cullis AG, Canham LT, Calcott PDJ. The structural and luminescence properties of porous silicon. *Journal of Applied Physics*. **1997**, 82, 909.

5. Chen Z, Lee T-Y, Bosman G. Electrical band gap of porous silicon. *Applied Physics Letters*. **1994**, 64, 3446.

6. Mentek R, Gelloz B, Koshida N. Photovoltaic Property of Wide-Gap Nanocrystalline Silicon Layers. *Japanese Journal of Applied Physics*. **2012**, 51, 02BP05.

7. Jarvis KL, Barnes TJ, Prestidge CA. Surface chemistry of porous silicon and implications for drug encapsulation and delivery applications. *Advances in Colloid and Interface Science*. **2012**, 175, 25–38.

8. Anglin EJ, Cheng L, Freeman WR, Sailor MJ. Porous silicon in drug delivery devices and materials. *Advanced drug delivery reviews*. **2008**, 60, 1266–1277.

9. Stewart MP, Buriak JM. Chemical and Biological Applications of Porous Silicon Technology. *Adv. Mater.* **2000**, 12, 859–869.

10. Sailor MJ, Wu EC. Photoluminescence-Based Sensing With Porous Silicon Films, Microparticles, and Nanoparticles. *Adv. Funct. Mater.* **2009**, 19, 3195–3208.

11. Kolasinski KW. Etching of silicon in fluoride solutions. Surface Science. 2009, 603, 1904–1911.

12. Lehmann V, Gösele U. Porous silicon formation: A quantum wire effect. *Applied Physics Letters*. **1991**, 58, 856.

13. Fang H, Li X, Song S, Xu Y, Zhu J. Fabrication of slantingly-aligned silicon nanowire arrays for solar cell applications. *Nanotechnology*. **2008**, 19, 255703.

14. Tian B, Kempa TJ, Lieber CM. Single nanowire photovoltaics. Chem. Soc. Rev. 2009, 38, 16–24.

15. Peng K-Q, Lee S-T. Silicon Nanowires for Photovoltaic Solar Energy Conversion. *Adv. Mater.* **2011**, 23, 198–215.

16. Hochbaum AI, Yang P. Semiconductor Nanowires for Energy Conversion. *Chem. Rev.* **2010**, 110, 527–546.

17. Wan J, Deng S-R, Yang R, u. a. Silicon nanowire sensor for gas detection fabricated by nanoimprint on SU8/SiO2/PMMA trilayer. *Microelectronic Engineering*. **2009**, 86(4–6), 1238–1242.

18. Leão CR, Fazzio A, da Silva AJR. Si Nanowires as Sensors: Choosing the Right Surface. *Nano Letters*. 2007, 7, 1172–1177.

19. Zhang GJ, Chua JH, Chee RE, u. a. Highly sensitive measurements of PNA-DNA hybridization using oxide-etched silicon nanowire biosensors. *Biosensors and Bioelectronics*. **2008**, 23, 1701–1707.

20. Chan CK, Peng H, Liu G, u. a. High-performance lithium battery anodes using silicon nanowires. *Nature Nanotech.* **2007**, *3*, 31–35.

21. Collins G, Holmes JD. Chemical functionalisation of silicon and germanium nanowires. *Journal of Materials Chemistry*. **2011**, 21, 11052.

22. Kayes BM, Atwater HA, Lewis NS. Comparison of the device physics principles of planar and radial p-n junction nanorod solar cells. *Journal of Applied Physics*. **2005**, 97, 114302.

23. Shao M, Ma DDD, Lee S-T. Silicon Nanowires – Synthesis, Properties, and Applications. *Eur. J. Inorg. Chem.* **2010**, 27, 4264–4278.

24. Schmidt V, Wittemann JV, Senz S, Gösele U. Silicon Nanowires: A Review on Aspects of their Growth and their Electrical Properties. *Adv. Mater.* **2009**, 21, 2681–2702.

25. Lee M, Jeon Y, Moon T, Kim S. Top-Down Fabrication of Fully CMOS-Compatible Silicon Nanowire Arrays and Their Integration into CMOS Inverters on Plastic. *ACS nano*. **2011**, 5, 2629-2636

26. Ozdemir B, Kulakci M, Turan R, Unalan HE. Effect of electroless etching parameters on the growth and reflection properties of silicon nanowires. *Nanotechnology*. **2011**, 22, 155606.

27. Peng K-Q, Yan Y-J, Gao S-P, Zhu J. Synthesis of Large-Area Silicon Nanowire Arrays via Self-Assembling Nanoelectrochemistry. *Advanced Materials*. **2002**, 14, 1164.

28. Zhang M-L, Peng K-Q, Fan X, u. a. Preparation of Large-Area Uniform Silicon Nanowires Arrays through Metal-Assisted Chemical Etching. *J. Phys. Chem. C.* **2008**, 112, 4444–4450.

29. Zhu J, Bart-Smith H, Begley MR, Zangari G, Reed ML. Formation of Silicon Nanoporous Structures Induced by Colloidal Gold Nanoparticles in HF/H2O2 Solutions. *Chemistry of Materials*. **2009**, 21, 2721–2726.

30. Chazalviel JN, Allongue P, Gouget-Laemmel A, u. a. Covalent Functionalizations of Silicon Surfaces and Their Application to Biosensors. *Science of Advanced Materials*. **2011**, 3, 332–353.

31. Mandler D, Kraus-Ophir S. Self-assembled monolayers (SAMs) for electrochemical sensing. *Journal of Solid State Electrochemistry*. **2011**, 15, 1535–1558.

32. Gooding JJ, Darwish N. The rise of self-assembled monolayers for fabricating electrochemical biosensors—an interfacial perspective. *Chem Record.* **2012**, 12, 92–105.

33. Masuda T, Fukumitsu H, Takakusagi S, u. a. Molecular Catalysts Confined on and Within Molecular Layers Formed on a Si(111) Surface with Direct Si–C Bonds. *Adv. Mater.* **2012**, 24, 268–272.

34. SHIMOMURA M. The New Trends in Next Generation Biomimetics Material Technology: Learning from Biodiversity. *Quaterly review*, **2010**, *37*, *53-75*

35. Dawood MK, Zheng H, Liew TH, u. a. Mimicking Both Petal and Lotus Effects on a Single Silicon Substrate by Tuning the Wettability of Nanostructured Surfaces. *Langmuir*. **2011**, 27, 4126–4133.

36. Vericat C, Vela ME, Benitez G, Carro P, Salvarezza RC. Self-assembled monolayers of thiols and dithiols on gold: new challenges for a well-known system. *Chemical Society Reviews*. **2010**, 39, 1805.

37. Haick H, Hurley PT, Hochbaum AI, Yang P, Lewis NS. Electrical characteristics and chemical stability of non-oxidized, methyl-terminated silicon nanowires. *Journal of the American Chemical Society*. **2006**, 128, 8990–8991.

38. Suspène C, Barattin R, Celle C, Carella A, Simonato J-P. Chemical Functionalization of Silicon Nanowires by an Electroactive Group: A Direct Spectroscopic Characterization of the Hybrid Nanomaterial. *The Journal of Physical Chemistry C.* **2010**, 114, 3924–3931.

39. Bashouti MY, Tung RT, Haick H. Tuning the Electrical Properties of Si Nanowire Field-Effect Transistors by Molecular Engineering. *Small*. **2009**, 5, 2761–2769.

40. Guo C-S, Luo L-B, Yuan G-D, u. a. Surface Passivation and Transfer Doping of Silicon Nanowires. *Angewandte Chemie International Edition*. **2009**, 48, 9896–9900.

41. He T, Ding H, Peor N, u. a. Silicon/Molecule Interfacial Electronic Modifications. J. Am. Chem. Soc. 2008, 130, 1699–1710.

42. Yuan GD, Zhou YB, Guo CS, u. a. Tunable Electrical Properties of Silicon Nanowires *via* Surface-Ambient Chemistry. *ACS Nano*. **2010**, 4, 3045–3052.

43. Pham VB, Tung Pham XT, Duong Dang NT, u. a. Detection of DNA of genetically modified maize by a silicon nanowire field-effect transistor. *Advances in Natural Sciences: Nanoscience and Nanotechnology*. **2011**, 2, 025010.

44. Paska Y, Stelzner T, Christiansen S, Haick H. Enhanced Sensing of Nonpolar Volatile Organic Compounds by Silicon Nanowire Field Effect Transistors. *ACS Nano*. **2011**, *5*, 5620–5626.

45. Vilan A, Yaffe O, Biller A, u. a. Molecules on Si: Electronics with Chemistry. Advanced Materials. 2010, 22, 140–159.

46. Walter MG, Warren EL, McKone JR, u. a. Solar Water Splitting Cells. *Chemical Reviews*. 2010, 110, 6446–6473.

47. Chen X, Lenhert S, Hirtz M, u. a. Langmuir–Blodgett Patterning: A Bottom–Up Way To Build Mesostructures over Large Areas. *Accounts of Chemical Research*. **2007**, 40, 393–401.

48. Ohgi T, Fujita D, Deng W, Dong ZC, Nejoh H. Scanning tunneling microscopy and X-ray photoelectron spectroscopy of silver deposited octanethiol self-assembled monolayers. *Surface science*. **2001**, 493, 453–459.

49. Petrovykh DY, Kimura-Suda H, Opdahl A, u. a. Alkanethiols on Platinum: Multicomponent Self-Assembled Monolayers. *Langmuir*. **2006**, 22, 2578–2587.

50. Haensch C, Hoeppener S, Schubert US. Chemical modification of self-assembled silane based monolayers by surface reactions. *Chem. Soc. Rev.* **2010**, 39, 2323–2334.

51. Tada A, Geng Y, Nakamura M, u. a. Interfacial modification of organic photovoltaic devices by molecular self-organization. *Physical Chemistry Chemical Physics*. **2012**, 14, 3713.

52. Gooding JJ, Ciampi S. The molecular level modification of surfaces: from self-assembled monolayers to complex molecular assemblies. *Chem. Soc. Rev.* **2011**, 40, 2704.

53. Sagiv J. Organized monolayers by adsorption. 1. Formation and structure of oleophobic mixed monolayers on solid surfaces. *Journal of the American Chemical Society*. **1980**, 102, 92–98.

54. Onclin S, Ravoo BJ, Reinhoudt DN. Engineering Silicon Oxide Surfaces Using Self-Assembled Monolayers. *Angewandte Chemie International Edition*. **2005**, 44, 6282–6304.

55. Hoffmann H, Mayer U, Krischanitz A. Structure of alkylsiloxane monolayers on silicon surfaces investigated by external reflection infrared spectroscopy. *Langmuir*. **1995**, 11, 1304–1312.

56. Brunner H, Vallant T, Mayer U, Hoffmann H. Formation of Ultrathin Films at the Solid–Liquid Interface Studied byIn SituEllipsometry. *Journal of Colloid and Interface Science*. **1999**, 212, 545–552.

57. Bierbaum K, Grunze M, Baski AA, u. a. Growth of Self-assembled n-alkyltrichlorosilane films on Si (100) investigated by atomic force microscopy. *Langmuir*. **1995**, 11, 2143–2150.

58. Vallant T, Brunner H, Mayer U, u. a. Formation of Self-Assembled Octadecylsiloxane Monolayers on Mica and Silicon Surfaces Studied by Atomic Force Microscopy and Infrared Spectroscopy. *J. Phys. Chem. B.* **1998**, 102, 7190–7197.

59. Tamura T, Adachi S. Photo-oxidation effects of light-emitting porous Si. Journal of Applied Physics. 2009, 105, 113518.

60. Zhong YL, Bernasek SL. Mild and efficient functionalization of hydrogen-terminated Si (111) via sonochemical activated hydrosilylation. *Journal of the American Chemical Society*. **2011**, 133, 8118–8121

61. Huck LA, Buriak JM. Towards a Mechanistic Understanding of Exciton-Mediated Hydrosilylation on Nanocrystalline Silicon. *Journal of the American Chemical Society*. **2012**, 134, 489–497.

62. de Smet LCPM, Zuilhof H, Sudhölter EJR, u. a. Mechanism of the Hydrosilylation Reaction of Alkenes at Porous Silicon: Experimental and Computational Deuterium Labeling Studies. *The Journal of Physical Chemistry B*. **2005**, 109, 12020–12031.

63. Holm J, Roberts JT. Thermally Induced Hydrosilylation at Deuterium-Terminated Silicon Nanoparticles: An Investigation of the Radical Chain Propagation Mechanism. *Langmuir.* **2009**, 25, 7050–7056.

64. Takeuchi N, Kanai Y, Selloni A. Surface reaction of alkynes and alkenes with H-Si (111): A density functional theory study. *Journal of the American Chemical Society*. **2004**, 126, 15890–15896.

65. Ng A, Ciampi S, James M, Harper JB, Gooding JJ. Comparing the Reactivity of Alkynes and Alkenes on Silicon (100) Surfaces. *Langmuir*. **2009**, 25, 13934–13941.

66. Scheres L, Giesbers M, Zuilhof H. Organic Monolayers onto Oxide-Free Silicon with Improved Surface Coverage: Alkynes versus Alkenes. *Langmuir*. **2010**, 26, 4790–4795.

67. Charlier J, Palacin S, Leroy J, u. a. Local silicon doping as a promoter of patterned electrografting of diazonium for directed surface functionalization. *Journal of Materials Chemistry*. **2008**, 18, 3136.

68. Buriak JM, others. Organometallic chemistry on silicon and germanium surfaces. *Chemical Reviews.* 2002, 102, 1271–1308.

69. Bashouti MY, Stelzner T, Christiansen S, Haick H. Covalent Attachment of Alkyl Functionality to 50 nm Silicon Nanowires through a Chlorination/Alkylation Process. *The Journal of Physical Chemistry C.* **2009**, 113, 14823–14828.

70. Seitz O, Böcking T, Salomon A, Gooding JJ, Cahen D. Importance of Monolayer Quality for Interpreting Current Transport through Organic Molecules: Alkyls on Oxide-Free Si. *Langmuir*. **2006**, 22, 6915–6922.

71. Vericat C, Vela ME, Benitez GA, u. a. Surface characterization of sulfur and alkanethiol self-assembled monolayers on Au (111). *Journal of Physics: Condensed Matter*. **2006**, 18, R867.

72. Chau TT, Bruckard WJ, Koh PTL, Nguyen AV. A review of factors that affect contact angle and implications for flotation practice. *Advances in Colloid and Interface Science*. **2009**, 150, 106–115.

73. Kwok DY, Neumann AW. Contact angle measurement and contact angle interpretation. *Advances in Colloid and Interface Science*. **1999**, 81, 167–249.

74. Nishino T, Meguro M, Nakamae K, Matsushita M, Ueda Y. The Lowest Surface Free Energy Based on –CF₃ Alignment. *Langmuir*. **1999**, 15, 4321–4323.

75. Neumann A., Good R., Hope C., Sejpal M. An equation-of-state approach to determine surface tensions of low-energy solids from contact angles. *Journal of Colloid and Interface Science*. **1974**, 49, 291–304.

76. Owens DK, Wendt RC. Estimation of the surface free energy of polymers. J. Appl. Polym. Sci. 1969, 13, 1741–1747.

77. Cassie ABD, Baxter S. Wettability of porous surfaces. Trans. Faraday Soc. 1944, 40, 546–551.

78. Banerjee S. Simple derivation of Young, Wenzel and Cassie-Baxter equations and its interpretations. *Arxiv preprint arXiv:0808.1460.* **2008**.

79. Brunner H, Mayer U, Hoffmann H. External reflection infrared spectroscopy of anisotropic adsorbate layers on dielectric substrates. *Applied spectroscopy*. **1997**, 51, 209–217.

80. Kattner J, Hoffmann H. External Reflection Spectroscopy of Thin Films on Dielectric Substrates. In: *Handbook of Vibrational Spectroscopy*. John Wiley & Sons, Ltd; **2001**.

81. Parikh AN, Allara DL. Quantitative determination of molecular structure in multilayered thin films of biaxial and lower symmetry from photon spectroscopies. I. Reflection infrared vibrational spectroscopy. *The Journal of Chemical Physics*. **1992**, 96, 927.

82. Diercks R, Dieck tom H. Diazadiene als Steuerliganden in der homogenen Katalyse, IX. Katalytische Cyclotetramerisierung von Propiolsäureestern. *Chem. Ber.* **1985**, 118, 428–435.

83. Ciampi S, James M, Michaels P, Gooding JJ. Tandem "Click" Reactions at Acetylene-Terminated Si(100) Monolayers. *Langmuir*. **2011**, 27, 6940–6949.

84. Abramof PG, Beloto AF, Ueta AY, Ferreira NG. X-ray investigation of nanostructured stainetched porous silicon. *Journal of Applied Physics*. **2006**, 99, 024304. 85. Ciampi S, Böcking T, Kilian KA, u. a. Functionalization of Acetylene-Terminated Monolayers on Si(100) Surfaces: A Click Chemistry Approach. *Langmuir*. **2007**, 23, 9320–9329.

86. Dumas P, Chabal YJ. Electron-energy-loss characterization of the H-terminated Si(111) and Si(100) surfaces obtained by etching in NH_4F . *Chemical Physics Letters*. **1991**, 181, 537–543.

87. Korotcenkov G, Cho BK. Silicon Porosification: State of the Art. *Critical Reviews in Solid State and Materials Sciences*. **2010**, 35, 153–260.

88. Turner DR. On the Mechanism of Chemically Etching Germanium and Silicon. J. Electrochem. Soc. 1960, 107, 810–816.

89. Schwartz B, Robbins H. Chemical Etching of Silicon. J. Electrochem. Soc. 1961, 108, 365–372.

90. Kelly MT, Chun JKM, Bocarsly AB. High efficiency chemical etchant for the formation of luminescent porous silicon. *Applied Physics Letters*. **1994**, 64, 1693.

91. Street RA, Qi P, Lujan R, Wong WS. Reflectivity of disordered silicon nanowires. *Applied Physics Letters*. **2008**, 93, 163109.

92. Mawhinney DB, Glass Jr JA, Yates Jr JT. FTIR study of the oxidation of porous silicon. *The Journal of Physical Chemistry B.* **1997**, 101, 1202–1206.

93. Yamada H, Imahori H, Nishimura Y, u. a. Photovoltaic Properties of Self-Assembled Monolayers of Porphyrins and Porphyrin–Fullerene Dyads on ITO and Gold Surfaces. *Journal of the American Chemical Society*. **2003**, 125, 9129–9139.

94. Scheres L, Arafat A, Zuilhof H. Self-Assembly of High-Quality Covalently Bound Organic Monolayers onto Silicon. *Langmuir*. **2007**, 23, 8343–8346.

95. Cicero RL, Linford MR, Chidsey CED. Photoreactivity of Unsaturated Compounds with Hydrogen-Terminated Silicon(111). *Langmuir*. **2000**, 16, :5688–5695.

96. Stewart MP, Buriak JM. Photopatterned Hydrosilylation on Porous Silicon. *Angewandte Chemie International Edition*. **1998**, 37, 3257–3260.

97. Sieval AB, Opitz R, Maas HPA, u. a. Monolayers of 1-Alkynes on the H-Terminated Si(100) Surface. *Langmuir*. **2000**, 16, 10359–10368.

98. Sieval AB, Demirel AL, Nissink JWM, u. a. Highly stable si-C linked functionalized monolayers on the silicon(100) surface. *Langmuir*. **1998** *14*, *1759-1768*.

99. Linford MR, Chidsey CED. Alkyl monolayers covalently bonded to silicon surfaces. *J. Am. Chem. Soc.* **1993**, 115, 12631–12632.

100. Yamamoto K, Masui A. TO-LO Splitting in Infrared Spectra of Thin Films. *Applied spectroscopy*. **1996**, 50, 759–763.

101. Sun XH, Wang SD, Wong NB, u. a. FTIR Spectroscopic studies of the stabilities and reactivities of hydrogen-terminated surfaces of silicon nanowires. *Inorganic chemistry*. **2003**, 42, 2398–2404.

102. Cao L, Price TP, Weiss M, Gao D. Super Water- and Oil-Repellent Surfaces on Intrinsically Hydrophilic and Oleophilic Porous Silicon Films. *Langmuir*. **2008**, 24, 1640–1643.

103. Liu Y, Yamazaki S, Yamabe S, Nakato Y. A mild and efficient Si (111) surface modification via hydrosilylation of activated alkynes. *Journal of Materials Chemistry*. **2005**, 15, 4906.

104. Imanishi A, Yamane S, Nakato Y. Si(111) Surface Modified with α,β -Unsaturated Carboxyl Groups Studied by MIR-FTIR. *Langmuir*. **2008**, 24, 10755–10761.

105. Qin G, Santos C, Zhang W, u. a. Biofunctionalization on alkylated silicon substrate surfaces via "click" chemistry. *Journal of the American Chemical Society*. **2010**, 132, 16432–16441.

106. Campos MAC, Paulusse JMJ, Zuilhof H. Functional monolayers on oxide-free silicon surfaces via thiol-ene click chemistry. *Chem. Commun.* **2010**, 46, 5512.

107. Fournier D, Hoogenboom R, Schubert US. Clicking polymers: a straightforward approach to novel macromolecular architectures. *Chem. Soc. Rev.* **2007**, 36, 1369.

108. Zhou C, Walker AV. Formation of Multilayer Ultrathin Assemblies Using Chemical Lithography. *Langmuir*. **2010**, 26, 8441–8449.

109. Jewett JC, Bertozzi CR. Cu-free click cycloaddition reactions in chemical biology. *Chem. Soc. Rev.* 2010, 39, 1272.

110. Burrows CJ, Muller JG. ChemInform Abstract: Oxidative Nucleobase Modifications Leading to Strand Scission. *ChemInform.* **1998**; 29.

111. Wang Q, Chan TR, Hilgraf R, u. a. Bioconjugation by Copper(I)-Catalyzed Azide-Alkyne [3 + 2] Cycloaddition. *J. Am. Chem. Soc.* **2003**, 125, 3192–3193.

112. Ciampi S, Le Saux G, Harper JB, Gooding JJ. Optimization of Click Chemistry of Ferrocene Derivatives on Acetylene-Functionalized Silicon(100) Surfaces. *Electroanalysis*. **2008**, 20, 1513–1519.

113. Leroux YR, Fei H, Noel J-M, Roux C, Hapiot P. Efficient Covalent Modification of a Carbon Surface: Use of a Silyl Protecting Group To Form an Active Monolayer. J. Am. Chem. Soc. **2010**, 132, 14039–14041.

114. Cai C, Yam CM, Gu J. Preparation of sensors on oligo- or poly(ethylene glycol) films on silicon surfaces. PCT Int. Appl. WO2009131891 A120091029. **2009.**

115. Boren BC, Narayan S, Rasmussen LK, u. a. Ruthenium-Catalyzed Azide–Alkyne Cycloaddition: Scope and Mechanism. *Journal of the American Chemical Society*. **2008**, 130, 8923–8930.

116. Himo F, Lovell T, Hilgraf R, u. a. Copper(I)-Catalyzed Synthesis of Azoles. DFT Study Predicts Unprecedented Reactivity and Intermediates. *J. Am. Chem. Soc.* **2004**, 127, 210–216.

117. Elamari H, Jlalia I, Louet C, u. a. On the reactivity of activated alkynes in copper and solvent-free Huisgen's reaction. *Tetrahedron: Asymmetry*. **2010**;21, 1179–1183.

118. Li Z, Seo TS, Ju J. 1,3-Dipolar cycloaddition of azides with electron-deficient alkynes under mild condition in water. *Tetrahedron Letters*. **2004**, 45, 3143–3146.

119. Limapichat W, Basu A. Reagentless functionalization of gold nanoparticles via a 3+ 2 Huisgen cycloaddition. *Journal of colloid and interface science*. **2008**, 318, 140–144.

120. Fleming DA, Thode CJ, Williams ME. Triazole Cycloaddition as a General Route for Functionalization of Au Nanoparticles. *Chem. Mater.* **2006**, 182327–2334.
121. Liu J, Paddon-Row MN, Gooding JJ. Surface reconstitution of glucose oxidase onto a norbornylogous bridge self-assembled monolayer. *Chemical Physics*. **2006**, 324, 226–235.

122. Liu G, Paddon-Row MN, Justin Gooding J. Protein modulation of electrochemical signals: application to immunobiosensing. *Chemical Communications*. **2008**, 33, 3870.

List of tables

Table 2.1. Overview of monolayer characterization methods	. 20
Table 2.2. Surface science techniques for characterization of SAMs.	.21
Table 3.1 Used chemicals	. 32
Table 3.2 . Reaction condition for adsorption of n- alkynes	. 37
Table 3.3 . Spectral parameters for the CH stretching absorptions of different alkyl groups based on literature data for octadecyl ⁵⁴	. 42
Table 4.1 Characteristics of Si(1000) before and after etching in 5% HF	. 46
Table 4.2 Etching of Si(100) wafer	. 46
Table 4.3 Characteristics of oxide free Si(100) wafer, porous silicon and silicon nanowire before and after hydrosilylation with octadecyne.	. 58

List of figures

Figure 1.1. Etching of Si(100) and Si(111) in fluoride solutions
Figure 1. 2. Proposed mechanism for anisotropic etching of silicon
Figure 1. 3 Schemtic figure illustrating the nanowire growth Vapour-liquid-solid (VLS) method by chemical vapour deposition (CVD)
Figure 1.4. Electroless etching of silicon nanowire9
Figure 1. 5. Some applications of self-assembled monolayers in nanotechnology
Figure 1. 6. Monolayer formation of trichlorosilanes adsorbed on silicon substrate covered with a native oxide
Figure 1. 7 Different approaches to form Si-C bonded monolayer
Figure 1.8 .: Hydrosilylation between a hydrogen terminated silicon surface and an alkyne or an alkene
Figure 1. 9. Hydrosilylation reaction mechanisms proposed by Buriak and co-workers 17
Figure 2.1. Schematic ilustration of the construction of an elipsometer
Figure 2.2. Contact angle of a liquid droplet wetted to an ideal solid surface
Figure 2.3. Young model, Wenzel model and Cassie-Baxter model
Figure 2.4. The contact angle for a defined θ as a function of surface roughness calculated with the Wenzel equation
Figure 2.5. The contact angle for a defined θ as a function of surface roughness calculated with the Cassie-Baxter equation,
Figure 2.6 Schematic illustration of the light in the RAIRS setup
Figure 2.7 a) Calculated reflectivity differences between the clean substrate (R0) and an isotropic adsorbate-covered substrate (Rs) on a silicon surfaceThe solid line correspond to p-polarized light and the dashed to s-polarized light. b) Calculated reflectivity differences between the clean substrate (R0) and an isotropic adsorbate-covered substrate (Rs) on a gold surface In (c) calculated absorbances - log Rs/R0 of the hypothetical adsorbate vibration at 3000 cm2 1 on a silicon surface as a function of the light incidence angle p-polarized radiation The light are denoted with Ax and Az represent the parallel and perpendicular x z components, respectively, of the total absorbance Ap, and u B is the Brewster angle. The same optical constants as in (a) were used for substrates and adsorbate
Figure 2.8. Long chain alkyne adorbed on a Silicon substrate

Figure 3.1. Reaction vessel used for hydrosilylation reactions 38
Figure 3.2 Seagull reflection unit used for reflection IR measurements
Figure 4.1. Schematic ilustration about the formation of H-terminated silicon substrate with different topologies
Figure 4.2 SEM image of prepared porous silicon
Figure 4.3. SEM images of inhomogeneous etched silicon nanowire on a silicon wafer. Image (a) is measured from a part of the wafer with a yellow appearance whereas image b is from a black part of the wafer. You can clearly see the correlation that black samples correspond to well aligned orthogonal silicon nanowire whereas a yellow colour indicates disorder and defects.
Figure 4.4. Si nanowire etched 30 min giving homogeneous well aligned silicon nanowires 50
Figure 4.5. SEM images of electroless etched silicon 24 h and 5 min respectively. The wafer that is etched 24 h yields wires up to 180 um however it is a defect uneven nanowire array. Wafer etched only 5 min yields about 3 um long nanowires, however they are also defect and partly bundled
Figure 4.6. Growth of silicon nanowire with metal catalysed chemical etching
Figure 4.7 . a) Transmission spectra of silicon nanowire etched 30 min, 1h and 2h min divided by the empty beamn. b) Single beam DRIFT spectrum of nanowire etched 30 min, 1h and 2h executed at an incidence angle of 15°
Figure 4.8. Si-H stretchings on hydrogenterminated a) flat silicon measured in RAIRS b) porous silicon c) silicon nanowire both measured tranmission
Figure 4.9. Transmission IR spectrum of H-terminated silicon nanowires before (a) and after (b) hydrosilylation with octadecyne
Figure 4.10. Different structural models of monolayers of octadecyne adsorbed on silicon surfaces. A)Anisotropic model with all-trans hydrocarbon chains. Note that the orientation of the terminal CH3 groups depends in this case on the sign of the tilt angle α . B) Mixed anisotropic/isotropic model with all-trans CH2 groups but randomly oriented CH3 chain termina. The methyl groups orientation is independent of the value and the sign of the chain tilt angle. C) Isotropic model with randomly oriented molecules
Figure 4.11 Experimental and simulated IR external reflection spectra of a high quality monolayer (d = 2.1 nm) of octadecyne adsorbed on Si (100) (p-polarized light, 81° incidence) a) experimental spectrum b) simulated spectrum for a fully anisotropic monolayer (model A) with a chain tilt angle of + 31° (solid line) and - 31° (broken line) c) simulated spectrum for a mixed anisotropic/isotropic monolayer (model B) with a 31° chain tilt angle d) simulated spectrum for a fully isotropic monolayer (model C)

Figure 4.12. a) Experimental octadecyne monolayer layer spectra of five different samples with thicknesses between 1.95 nm and 2.1 nm Simulated octadecyne monolayer spectra as in Fig. 4.11 c) (model B) for three different chain tilt angles $\alpha = 28^{\circ}$, 31° and 34°......61

Figure 4.13. Experimental and simulated IR spectra of lower quality monolayers of octadecyne on Si (100). The simulated spectra were calculated as mixtures of ordered (model B) and disordered (model C) domains: a) 74 % ordered b) 59% ordered64

Figure 4.18 Contact angle measurements of H-terminated and octadecyne coated silicon	
substrates exposed to 60°C in an oven	. 69

Figure 4.19. Stability of coated and uncoated silicon nanowire in alkaline solution (R.T. pH12)......71

Figure 4.20. RAIRS spectra of tetradecanolpropiolate (solid line) and pentadecyne (dotted	
line) adsorbed on a Si(100) wafer.	.73

Figure 4.21 IR spectra of different silicon substrates modified with TDP, DDDP and EDDP a) silicon nanowires b) flat polycrystalline silicon (ATR crystal) c) and porous silicon........75

Figure 4.26. Schematic figure of nanadiyne adsorbed on porous silicon and silicon nanowire. The inhomogeneous morphology and concave surface geometry of porous silicon enable diynes to bind with both terminal alkyne groups to the substrate
Figure 4.27. Water contact angle and Infrared spectra of surface-modified silicon nanowires:(a) hydrogen-terminated SiNW, (b) after hydrosilylation of (a) with 1,2-ethanediol dipropiolate, and (c) after click reaction of (b) with 1-azidooctane
Figure 4.28. Click reaction of activated and non-activated alkynes adsorbed on Si nanowires with 1-azidooctane 85
Figure 4.29. Surface click coupling of different target functionalities onto silicon nanowires primed with ethandiol dipropiolate (EDDP)
Figure 4.30. Infrared spectra of surface-modified silicon ATR crystals. Top: a hydrogen- terminated ATR crystal. Middle: after hydrosilylation with 1,2-ethanediol dipropiolate Bottom: after click reaction of with 1-azidooctane
Figure 4.31. IR spectra of (hept-6-ynyl 3-(trimethylsilyl)propiolate adsorbed on silicon nanowires. a) Freshly adsorbed b)after 1 min deprotection in ethanol saturated with K ₂ CO ₃ . c) after 5 min deprotection c) After 10 min deprotection d) After 20 min deprotection.