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Organic Surface Modification of Silicon Nanowire-Based Sensor Devices

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1. Introduction

The year 2011 marks the 10th anniversary of silicon nanowire (SiNW)-based electronic devices. Since their introduction (Cui & Lieber, 2001) SiNW-based sensor devices have gained considerable interest as a general platform for ultra-sensitive, electrical detection of biological and chemical species (Figure 1). Although SiO_x coatings can be used for the detection of protons (Cui, 2001), and gases (Wan, 2009), the specific detection of other analytes, including ions and biomolecules requires the presence of an affinity layer that interacts with the analyte of interest. Such a layer can be added on top of the nanowire by the modification of the nanowire surface. In this chapter we review the surface modification strategies that have been explored on SiNW-based devices over the past decade.
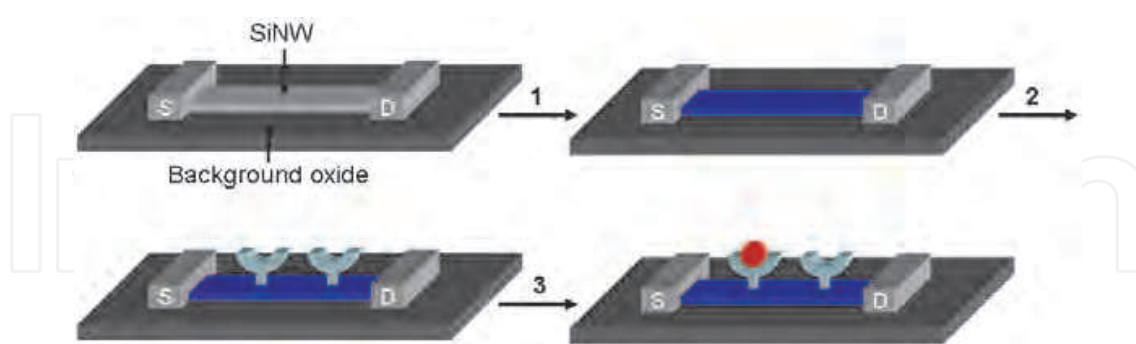

Fig. 1. Schematic representation of a SiNW-based device (top left), of which the nanowire has been chemically modified (step 1), followed by the immobilization of receptors (step 2) and the binding of an analyte (step 3). S and D stand for source and drain, respectively.

1.1 Scope and organization of this review chapter

This chapter focuses on surface modification strategies of SiNW-based devices. Our review concentrates on electrical devices that consist of in-plane orientated SiNWs, which are positioned between two ohmic contacts, often referred to as source and drain.

For an extensive overview of different materials that have been explored to prepare NW-based sensors, including silicon, we refer to the review of Ramgir et al. (Ramgir, 2010).

Several reviews on SiNW-based devices have been written with a clear focus on the chemical-vapour-deposition fabricated NWs by the Lieber and Zhou groups (Li, 2006; Patolsky, 2006b; Carlen & van den Berg, 2007) or top–down fabricated SiNW-based sensors from the Reed group (Stern, 2008). In this chapter we will discuss issues related to the modification of SiNW-based devices with organic compounds. The topics of SiO_x (Aswal, 2006) and Si-H (Aswal, 2006; Stutzmann, 2006; Hamers, 2008) surface modification with covalently linked organic monolayers have been reviewed extensively. However, the main focus of these reviews is on the modification of large planar substrates, while the focus if this chapter is on SiNW-based devices. A review by Wanekaya et al. contains a paragraph on the covalent functionalization of SiNWs with biomolecules (Wanekaya, 2006). Very recent reviews also include sections with brief schemes for SiNW functionalization (Shao, 2010; Tey, 2010).

In this chapter we aim to give an overview of all the different surface modification strategies that have been explored to modify SiNW-based devices, including non-covalent immobilization strategies. The methods can be divided into different categories (Table 1). The first one is based on silanization chemistry, i.e., the reaction between hydroxyl-terminated surfaces and organosilanes. Also other compounds like activated esters or organophosphonates have been covalently attached to SiO_x surfaces. In addition, polyelectrolytes and bilayers have been physically adsorbed onto SiO_x surfaces. The last approach follows the route of oxide removal, followed by the reaction with (ω-functionalized)-1-alkenes.

Surface	Modification Method	Type of Binding	Nature Film	# Papers (Year of First Report)	§
SiO_x	Silanization	Covalent	Monolayer	>50 (2001)	2.1.1
SiO_x	Esterification	Covalent	Monolayer	1 (2004)	2.2
SiO_x	Phosphorization	Covalent	Monolayer	1 (2008)	2.2
SiO_x	Layer-by-Layer	Electrostatic	Multilayers	1 (2010)	2.3.1
SiO_x	Lipid membrane	Electrostatic	Bilayer	2 (2009)	2.3.2
Si-H	Hydrosilylation	Covalent	Monolayer	6 (2006)	3

Table 1. Overview of different strategies used in the modification of SiNW-based devices.

## 2. SiO_x-covered SiNW-based sensor devices

Cleaned silicon surfaces exposed in an ambient environment such as air or solutions will oxidize spontaneously (Zhang, 2001b). The silicon oxide layer, in this chapter referred to as SiO_x –either native oxide or oxide grown under controlled conditions–, passivates the silicon surface. This allows the silicon to be used as an electronic material in processing and application environments. After fabrication, or at least after exposure to ambient environment, also SiNWs contain a SiO_x layer. Typically the thickness of this SiO_x layer on the NW is 1.5-10 nm, whereas the background oxide is usually >10 nm. It is important to note that –in terms of surface modification– one cannot discriminate between the oxide of the nanowire and background oxide; both are modified. The surface modifications described in §2 deal with SiO_x-coated SiNW devices.

2.1 Covalent functionalization
2.1.1 Silanization

The most applied method to functionalize silica surfaces is through the self-assembly of organofunctional alkoxysilane and chlorosilane molecules. While early silane-based monolayer work is based on Langmuir-Blodgett techniques, the first silane-based self-assembled monolayer was reported by Sagiv in 1980 (Sagiv, 1980). In general, a hydroxylated surface is introduced into a solution of a silane derivative in an organic solvent, but gas-phase methods have also been used (Aswal, 2006). In all cases, thorough cleaning of the substrate is a must for obtaining a clean and activated (hydroxylated) oxide layer with a high density of silanol groups on the surface (~ 10^{15} per cm^2) (Aswal, 2006). Scheme 1 gives a schematic representation of the formation of a silane monolayer onto SiO_x surfaces. It should be noted that this chemistry is not limited to SiO_x surfaces; other hydroxylated oxides surfaces can be modified as well (e.g., Al_2O_3 (Wang, 2008)).

Also in the case of the surface functionalization of the SiO_x surfaces of SiNW-based devices the most applied method is silanization. Figure 2 gives an overview of the different silane derivatives that have been used, while Table 2 gives a number of examples of surface silanization, together with the target analytes. It should be noted that on planar SiO_x substrates more compounds have been used; here we aim to give an overview for SiNW-based devices only. Table 2 summarizes the first papers on SiNW-based sensor devices and selected papers that use other silanization methods. We have categorized the references in terms of pH sensors, biosensors, cation sensors and gas sensors. This way, the cited work does not only represent the diversity of silane compounds that have been used, it also shows the variation in the further (bio)functionalization of SiNW-based devices.
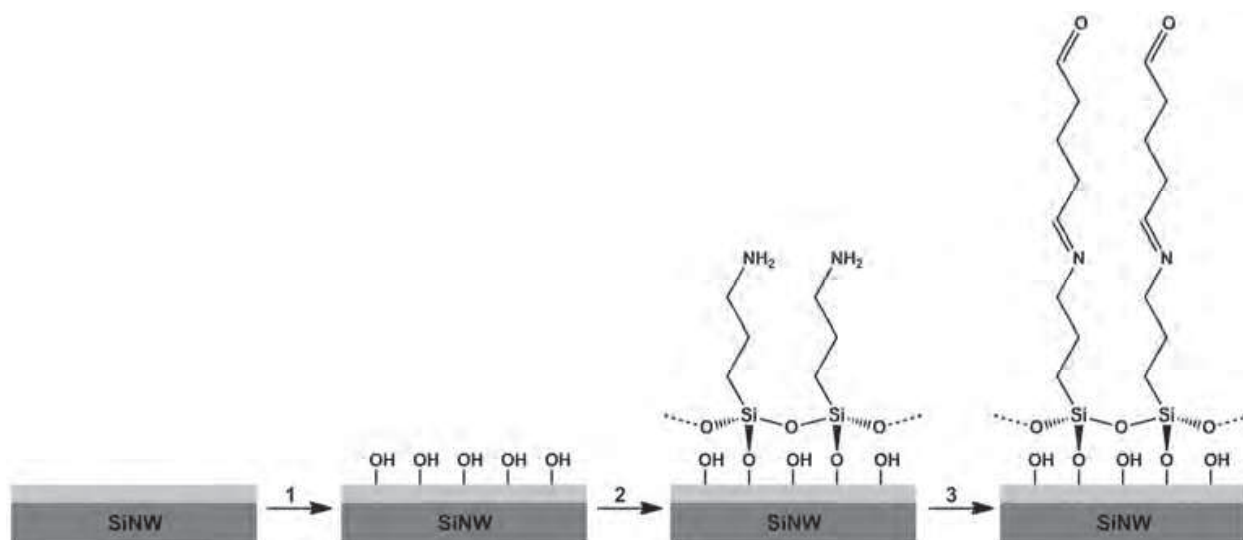
Scheme 1. Schematic representation of the 1) cleaning/hydroxylation of the SiO_x surface, 2) silanization (here: silane 1a, Figure 2), and 3) further functionalization with glutaraldehyde. It should be noted that the exact structure of the bonded silanes is arbitrary as also two or three silanol groups per attached molecule may react with the surface hydroxyl groups. Here we adapted the scheme from Aswal et al. (Aswal, 2006).

Sensor Type	Surface Modification*		Receptor	Analyte	Reference
pH	SiO$_2$			H$^+$	
	APTES (**1a**)			H$^+$	(Cui, 2001; Bunimovich, 2006; Chen, 2006)
	APTES (**1a**)		DNA-templated polymerization of aniline	H$^+$	(Ma, 2004)
Bio `			Biotin	Streptavidin	(Cui, 2001)
	APTES (**1a**)		15-mer ss-DNA	Hybridization-induced charges in poly-T/poly-A 15-mer DNA	(Lin, 2007)
	APDMES (**1b**)		16-mer ss-DNA	Complementary DNA	(Bunimovich, 2006)
	MPTMS (**4a**)		12-mer ss-DNA	Single mismatch	(Li, 2004)
	APMS (**3**)		Monoclonal antibodies	PSA	(Zheng, 2005)
	APMS (**3**)		Antibody	influenza	(Patolsky, 2004)
	APMS (**3**)		Tyrosine kinase	ATP	(Wang, 2005)
	APTES (**1a**)	GA	Estrogen receptors protein	Estrogen response elements	(Zhang, 2010)
	APTES (**1a**)	GA	Anti-PSA	PSA	(Kim, 2007)
	APTES** (**1a**)	GA	Glucose oxidase	Glucose	(Wang, 2008)
	APTES (**1a**)	GA	Anti-CRP	CRP	(Lobert, 2003; Patolsky, 2006a)
	APTES (**1a**)		EDC-supported carboxy-phenylboronic acid (CPBA)	Dopamine	(Li, 2010)
	AEAPS (**2**)		Gold nanoparticles	Thiol-terminated enzyme	(Sheu, 2005)
Cations	SiO$_2$		Calmodulin	Ca^{2+}	(Cui, 2001)
	MPTES (**4b**)			Hg$^+$, Cd$^+$	(Luo, 2009)
	AEAPS (**2**)	GA	(phosphor)tyrosine	Ca^{2+}	(Bi, 2008b)
	APMS (**3**)		Gly-Gly-His	Cu^{2+}	(Bi, 2008a)
Gas	APTES (**1a**)			TNT	(Engel, 2010)

Table 2. Examples of surface modifications on SiO$_x$-covered SiNW devices and target analytes.

GA = Glutaraldehyde; EDC = 1-Ethyl-3-[3-dimethylaminopropyl]carbodiimide hydrochloride; PSA = Prostate specific antigen; ATP = Adenosine triphosphate; TNT = Trinitrotoluene; CRP = C-reactive protein; * The chemical structures of the silanes are given in Figure 2; ** The silicon nanowires are covered with a layer of 10 nm Al$_2$O$_3$, grown by atomic layer deposition.
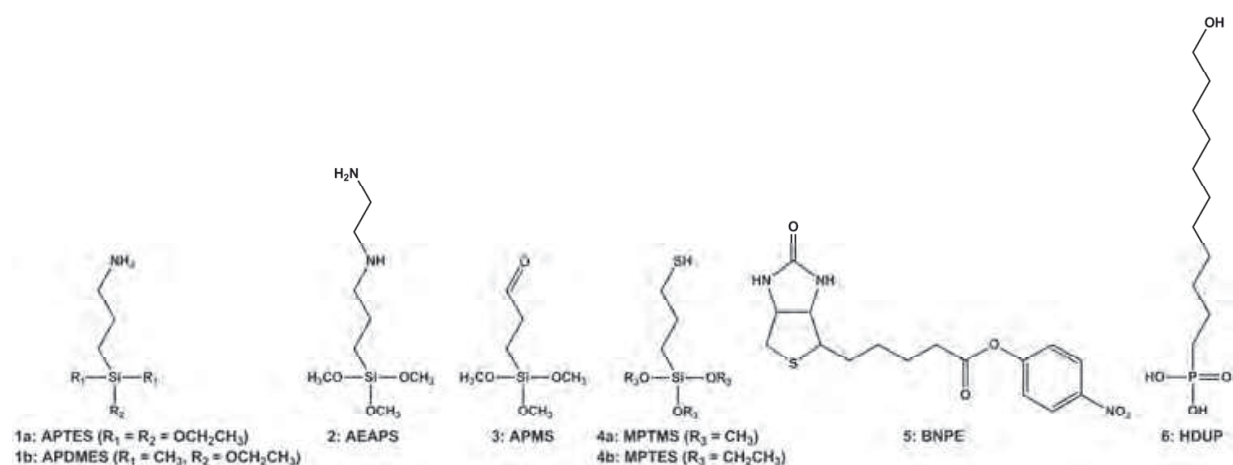
Fig. 2. Compounds that have been used in the modification on SiO$_x$-coated NWs in NW-based devices: 3-aminopropyltriethoxysilane (APTES, 1a), (3-aminopropyl)-dimethyl-ethoxysilane (APDMES, 1b), *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEAPS, 2), 3-aldehydepropyltrimethoxysilane (APMS, 3), mercaptopropyltrimethoxysilane (MPTMS, 4a), mercaptopropyltriethoxysilane (MPTES, 4b), biotin 4-nitrophenyl ester (BNPE, 5) and 11-hydroxyundecyl-phosphonate (HUP, 6).

2.1.1.1 3-Aminopropyltriethoxysilane

The first paper of the Lieber group on SiNW-based devices shows the utilization of silane-based functionalization of SiO$_x$-coated nanowires (Cui, 2001). The devices were chemically modified with 3-aminopropyltriethoxysilane (APTES, Figure 2, silane **1a**). The resulting devices showed a linear source-drain conductance versus pH-response for pH values from 2 to 9. The authors explained these results by the presence of both NH$_3^+$ and SiOH groups, which have different acid dissociation constants. At low pH, the amino group is protonated, and acts as a positive gate, which depletes hole carriers in the p-type SiNW and decreases the conductance. At high pH, the SiOH group is deprotonated, causing an increase in conductance. Ma et al. realized pH sensitivity via the enzymatic polymerization of aniline, which was templated by DNA on APTES (Ma, 2004) (Figure 3). The direct use of the stretched, immobilized DNA molecules as templates prevents the agglomeration of the polyaniline/DNA complexes formed in solution.
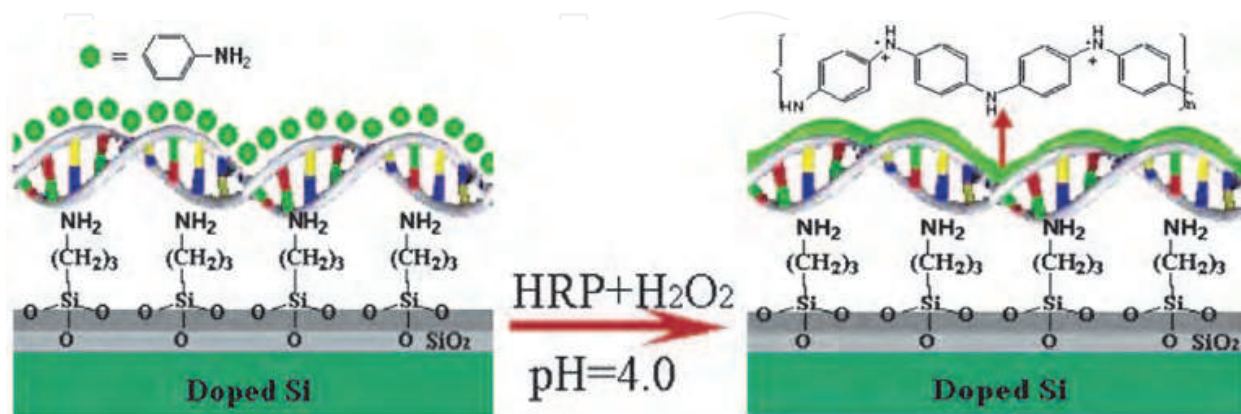

Fig. 3. Fabrication of a polyaniline nanowire immobilized on a SiO$_x$ surface with stretched double-stranded DNA as a guiding template, resulting in pH sensitivity. HRP stands for horseradish peroxidase. Figure from (Ma, 2004) reprinted with permission from the American Chemical Society ©.

Besides its use as sensitive layer in the detection of protons, recently APTES has also been used as a sensing layer for the vapor-phase detection of 2,4,6-trinitrotoluene (TNT) (Engel, 2010). The sensing mechanism is based on the acid-base interaction between the amino-terminated nanowire surface and the polarized TNT nitro groups, which have a weak basicity. The binding of electron-deficient TNT molecules to the amino groups on the SiNW sensor surface is believed to result in the formation of charge-transfer complexes, which act as effective molecular gating elements. The conductance response of the resulting devices has a clear relation with the concentration of the explosive analytes and the device was found to be able to distinguish the target analyte from structurally related compounds. This example nicely shows that SiNW-based sensors are not only sensitive to changes in charges, but also to changes in charge density.

Given its reactivity towards aldehyde, carboxylic acid and epoxy functionalities, APTES has become the most frequently used linker compound for further (bio)functionalization of SiNWs. The activation procedure of the SiO_x nanowire surface using an oxygen plasma, followed by the immersion in a solution of APTES in ethanol and subsequent heating of the chip as reported by the Lieber group (Cui, 2001) is commonly used (Patolsky, 2006a; Wang, 2008). Alternative approaches have been reported as well, e.g., the use of UV/ozone for the surface activation, followed by the use of neat APTES (Li, 2010). Also toluene (Lobert, 2003) and acetone (Lin, 2007) have been used as a solvent in the silanization step.

Because of the possibility of hydrogen bond formation between the amine of APTES and the SiO_x surface, both head and tail groups can be oriented towards the surface, which can result in a large disorder in APTES layers (Vandenberg, 1991). Additionally, cross-linking between the alkoxy silane units may yield oligomerized silane structures on the surface, resulting in rough layers that are thicker than a monolayer. The optimal conditions for solvent-based silanization using APTES were investigated on planar surfaces (Howarter & Youngblood, 2006). The morphology and growth kinetics of APTES films deposited from solutions were found to be affected by reaction time, solution concentration, and temperature. Experiments with an APTES concentration of 1% only produced good films when the reaction was time-limited (1 h). Increasing the reaction time increased the APTES film thickness.

To overcome the problem of the disordered monolayers, Lin et al. performed a post-treatment of APTES-functionalized devices (Lin, 2007). After the APTES modification, they aligned the internal dipoles of the APTES molecules using high electric fields, thus decreasing the disorder in the monolayer. In addition, it is shown that the source-drain conductance of the APTES-functionalized devices changes upon UV illumination. The authors explained this by a strengthening effect of the internal APTES dipoles by UV illumination. Additionally, UV illumination excites extra charge carriers in the nanowire. Depending on the size of both effects, the resistance of the nanowire can be increased or decreased, which was found to be measurable with the produced devices.

A modification that often follows the attachment of APTES to the SiO_x nanowire surface is the reaction with glutaraldehyde (GA, Scheme 1, right). This linker molecule is used to form an aldehyde-terminated surface, which increases the possibilities for further reactions, including the reaction with amine groups of, e.g., anti-bodies (Kim, 2007), proteins and enzymes (Lee, 2008; Wang, 2008; Zhang, 2010). Also amino-terminated, single-stranded DNA (ss-DNA) has been attached to APTES/GA-modified surfaces to measure hybridization-induced mismatches in 15-mer ss-DNA chains (Lin, 2007). The addition of glutaraldehyde is, like that of APTES, both performed from solution (Bi, 2008b; Zhang, 2010) and from the gas phase (Wang, 2008).

Li et al. reported the functionalization of an APTES-coated thin oxide gate with a dopamine receptor (Li, 2010). Although the devices do no belong to the class of SiNW-based sensors, the CMOS open-gate Field-Effect Transistor (FET) devices have (sub)micrometer gate dimensions. They have immobilized carboxyphenylboronic acid onto the APTES layer. The boronic acid group specifically reacts with the catechol functionality of, e.g., dopamine, which was detected in the femtomolar range.

2.1.1.2 Other silane derivatives

Apart from APTES, also other amino-terminated silane derivatives have been used. For example, (3-aminopropyl)-dimethyl-ethoxysilane (APDMES, Figure 2, silane **1b**) has been used in the modification of SiNW-based devices to bind a 16-mer ss-DNA (Bunimovich, 2006). In contrast to APTES (**1a**), APDMES (**1b**) is a mono-alkoxydimethylsilane, which is a crucial difference when it comes to the monolayer quality. Although silanes with only alkoxy group can react with each other, oligomerization can not take place. Consequently, the use of mono-alkoxydimethylsilanes results in the formation of a true monolayer. Very recently this issue was addressed in a detailed study by Dorvel et al. who synthesized an amino- and an epoxy-terminated mono-alkoxydimethylsilane, which were immobilized onto planer silicon oxide surfaces (Dorvel, 2010).

In addition, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEAPS, Figure 2, silane **2**) has been applied to immobilize an amino acid (Bi, 2008b). The nanowires devices were exposed to a solution of AEAPS in water, subsequently washed and finally dried to stimulate cross-linking of the molecules. This was followed by the reaction with GA to produce an aldehyde-terminated surface. Finally, tyrosine and phosphotyrosine were cross-linked with the aldehyde group through the formation of a Schiff base, which was further reduced to a stable secondary amine using sodium cyanoborohydride (NaBH$_3$CN). The studies, however, do not contain information on potential benefits of the alternative silanization agents used.

Some other functionalities rather than amino groups have been employed in silane chemistry (Figure 2, silanes 3 and 4). Apart from APTES, the Lieber group used 3-aldehydepropyltrimethoxysilane (APMS, Figure 2, silane 3) (Zheng, 2005) to directly obtain an aldehyde-terminated surface. Subsequently, monoclonal antibodies were attached to detect prostate specific antigens (PSA). The use of APMS enabled them to make a thinner organic layer as compared to combining APTES with glutaraldehyde. As oxygen in air will slowly oxidize aldehydes to acids or peracids, it is advisable to work with freshly prepared APMS surfaces or to make use of the reaction of glutaraldehyde with an APTES surface, directly prior to further functionalization.

As a last example we mention the use of 3-mercaptopropyltriethoxysilane (MPTES, Figure 2, silane **4b**) (Luo, 2009), which was applied to detect Cd^{2+} and Hg^{2+} ions. The thiol-terminated devices showed a linear relation between the logarithm of the Cd^{2+} and Hg^{2+} concentration and the source-drain conductance. The response towards K$^+$, Na$^+$, Ca^{2+}, Ba^{2+}, and Mg^{2+} (hard Lewis acids) was considerably smaller as compared to Cd^{2+} and Hg^{2+} (soft Lewis acids). This difference can be explained by the chemical softness of thiol groups, which hardly coordinate with hard Lewis acids.

2.1.2 Alternative approaches

In this paragraph we address two different types of non silane-based compounds that have been used in the chemical modification of SiO$_x$ surfaces of SiNW-based devices. Hahm and Lieber report on the 4-(dimethylamino)pyridine (DMAP)-catalyzed transesterification of biotin 4-nitrophenyl ester with the hydroxyl groups of SiO$_x$ nanowire surface (Hahm & Lieber, 2004)

(Figure 4, left). Afterwards, the devices were exposed to phosphate-buffered saline (PBS) solution of avidin, which was followed by the addition of biotinylated peptide nucleic acid (PNA) capture probes. A generally benefit of the use of PNA over DNA is that it enables sensing in an ultra-low background due to the lack of charges on the peptide backbone. In the work of Hahm and Lieber the surfaces were not analyzed after each modification step. However, based on the electrical characteristics of the modified devices it can be concluded that the PNA immobilization was successful. It has to be noted though that siloxane ester bonds (Si-O-(CO)) have a limited hydrolytic stability, at least lower than in the case of siloxane bonds (Si-O-Si). As a result, this immobilization technique is not often used.

Cattani-Scholz et al. investigated hydroxyalkylphosphonate monolayers as a platform for the biofunctionalization of SiNW-based field effect sensor devices (Cattani-Scholz, 2008) (Figure 4, right). They employed a stepwise functionalization protocol using 11-hydroxyundecylphosphonate and a maleimide heterobifunctional linker system. The surface chemistry was also performed on planar surfaces, which made it possible to extensively analyze the surfaces after each step. It was found that the hydroxyalkylphosphonate monolayer effectively passivates the Si surface against electrochemical leakage current into the electrolyte solution through the interface, with maximum currents of the order of 10 pA measured at an applied voltage of 200 mV. In a comparative study it has been shown that phosphonate monolayers on the native oxide of Ti-6Al-4V are hydrolytically more stable than the corresponding siloxane monolayers (Silverman, 2005). It is also reported that the monolayer growth is not limited by the surface OH content,(Hanson, 2003) making this type of surface modification an interesting alternative for silane-based chemistry.
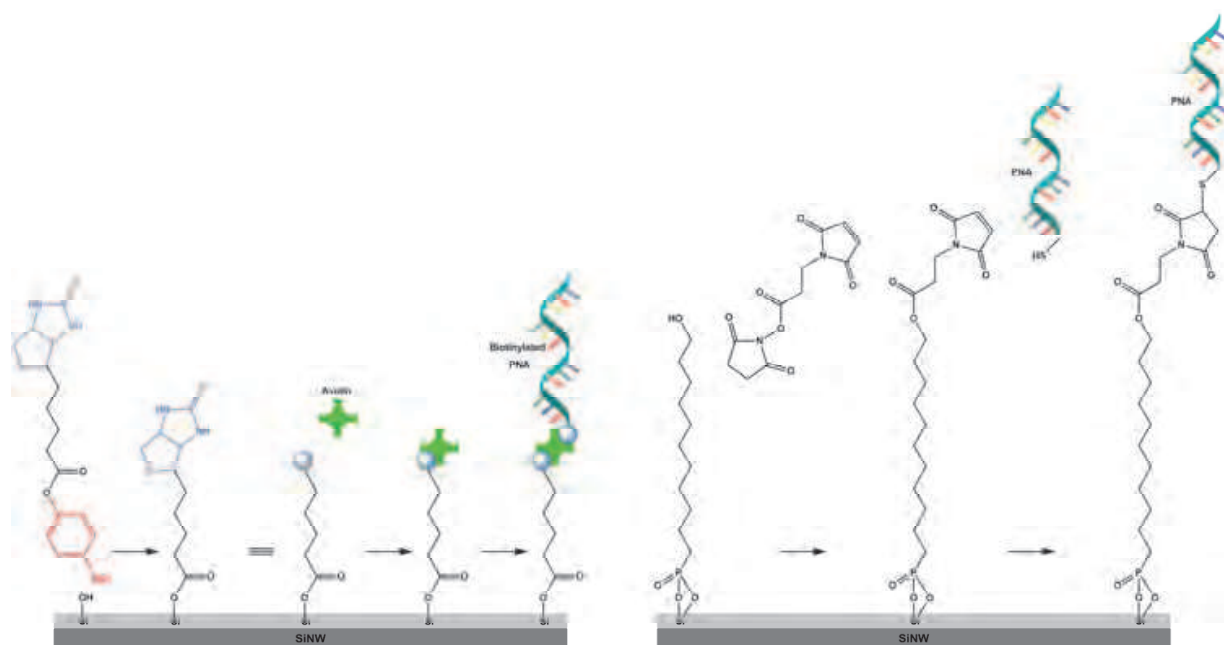

Fig. 4. A schematic representation of two different surface chemistries that have been used to attach PNA onto SiO$_x$: (left) the use of biotin 4-nitrophenyl ester (the blue part of the structure indicates biotin molecule, whereas the red part of the structure indicates the 4-nitrophenyl group, which is used to activate the ester), the following steps involve the use of avidin and biotinylated PNA, and (right) the formation of organophosphonate monolayer, followed by the reactions with a maleimide heterobifunctional linker and subsequently with a thiolated PNA derivative.

2.2 Non-covalent functionalization
2.2.1 Adsorption of polyelectrolytes

The negative nature of SiO_x at pH > 3.5 allows one to electrostatically immobilize positively charged polymers (polycations), also called generally polyelectrolytes (PEs). Subsequently, a negatively charged polymer (polyanion) can be adsorbed on top. Providing that each adsorption step of charged polymers leads to a charge inversion of the surface (charge overcompensation effect), the subsequent deposition finally results in a PE multilayer, stabilized by strong, multivalent electrostatic forces. This method is known as layer-by-layer (LbL) deposition (Decher, 1997). A variety of deposition methods can be used, including dip-coating, spin-coating, spray-coating and flow-based techniques.

Recently Ingebrandt and coworkers applied the LbL deposition technology onto SiNW-based devices (Vu, 2010). They immobilized polyallylamine hydrochloride (PAH: MW 15,000) onto 6 nm thick, thermally grown SiO_x via dip coating. Subsequently, polystyrenesulphonate (PSS: MW 60,000-80,000) was immobilized and this sequence was repeated several times to make a stack of 6 bilayers (Figure 5). The thickness of the resulting multilayer has not been reported. Assuming a monolayer thickness of ~ 2 nm (Decher, 1997; Poghossian, 2007) the multistack thickness would be ~ 24 nm. It has to be noted, however, that the salt concentration has an effect on the layer thickness (Decher & Schmitt, 1992), which makes it difficult to predict the thickness accurately. Although the noise level of PE-coated devices was slightly higher than that of their standard FET devices, the sensitivity for PE adsorption measurements was 3 to 4 times higher as compared to previous reports.
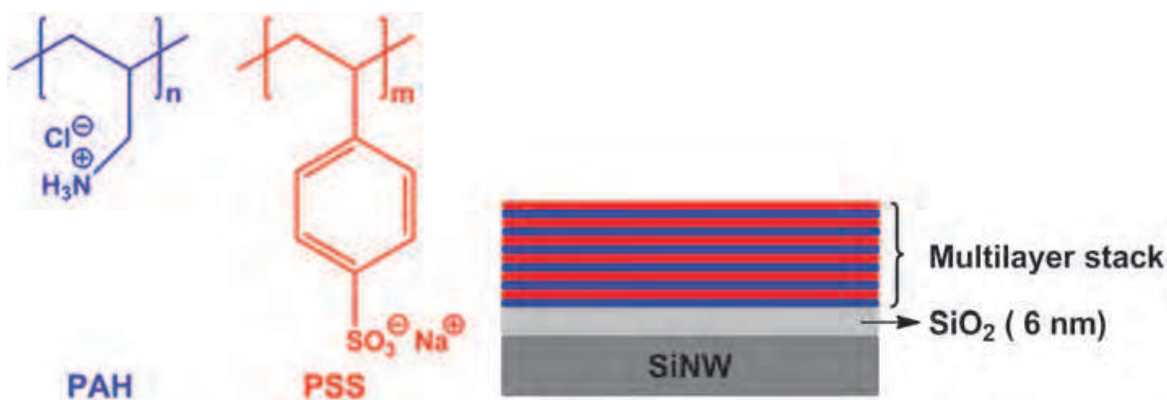

Fig. 5. Structures of the polycation polyallylamine hydrochloride (PAH) and polyanion polystyrenesulphonate (PSS) used by Ingebrandt and coworkers to prepare layer-by-layer multilayers onto SiO_x-covered SiNW-based devices.

2.2.2 Lipid membranes

Silica surfaces have also been used as a platform to immobilize model membrane systems like supported lipid bilayers, which have been extensively used in understanding the fundamental properties of biological membranes. However, there have been only a few attempts to apply lipid membranes on nanoelectronic devices. Misra et al. incorporated lipid bilayer membranes into SiNW transistors (Figure 6). In more detail, they covered the NWs and the background oxide with a continuous lipid bilayer shell, forming a barrier between the SiO_x surface and solution species (Martinez, 2009; Misra, 2009). The method is based on the fusion of spherical unilamellar vesicles onto a SiNW surface producing a planar conformal lipid bilayer coating (Huang, 2007).
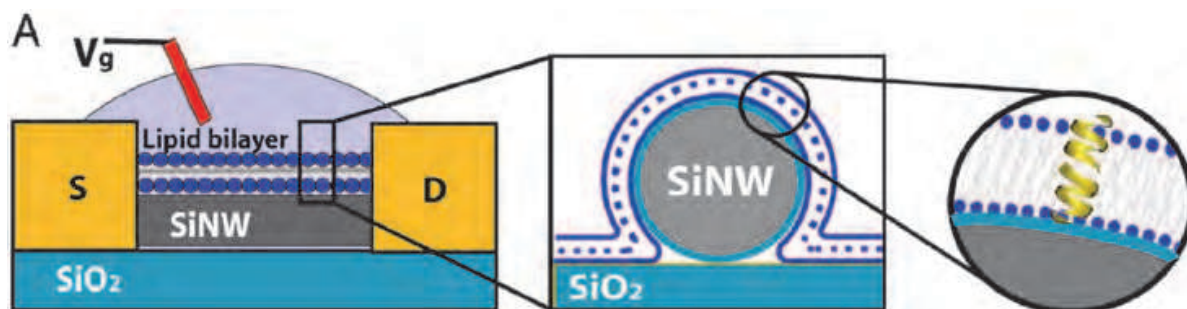
Fig. 6. Device schematics showing a SiNW connected to microfabricated source (S) and drain (D) electrodes. Although this is not clear from the figure it should be noted that the source and drain are insulated with Si₃N₄. The insets show the configuration of the lipid bilayer and a pore channel placed in the bilayer membrane. Figure from (Misra, 2009) reprinted with permission from National Academy of Sciences, USA.

Cyclic voltammetry using potassium ferrocyanide ($K_4Fe(CN)_6$) as a redox probe showed that the presence of a lipid bilayer on the NW surface reduced the limiting current by 85–95% relative to the native oxide-covered NW device (Misra, 2009). Subsequently, two different transmembrane peptides (gramicidin A and alamethicin) were incorporated in the vesicles, resulting in ion channel-containing lipid bilayers after fusion with SiNW-based devices. It was shown that the incorporation of transmembrane peptide pores enabled ionic-to electronic-signal-transduction by using voltage-gated and chemically gated ion transport through the membrane pores.

3. Oxide-free SiNW-based sensor devices

3.1 Hydrosilylation

As an alternative to silane-based chemistry, silicon substrates can also be modified using so-called hydrosilylation chemistry, e.g., the reaction between a surface Si-H and an organic compound containing a terminal unsaturated carbon-carbon bond (alkenes and alkynes) to form a Si-C linked monolayer (Scheme 2).
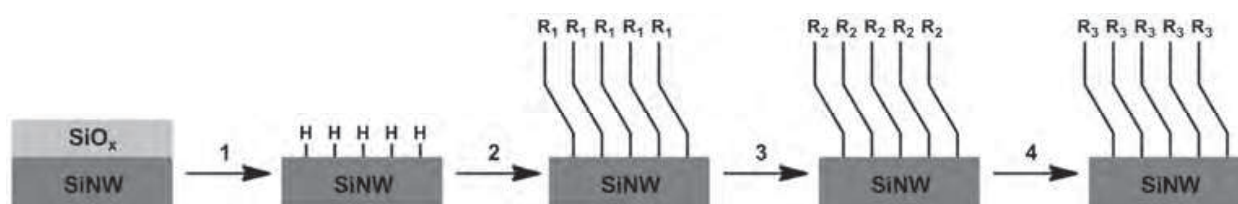
Scheme 2. Schematic representation of the 1) etching of the SiO$_x$ surface, yielding a H-terminated surface, 2) formation of Si-C monolayers via hydrosilylation (R$_1$ represents a functional group that is chemically protected towards the reaction with the H-terminated Si surface, e.g., an ester or amide), 3) deprotection the functional group (represented by R$_2$, e.g., a carboxylic acid or amine), 4) attachment of a receptor (represented by R$_3$).

This work has been pioneered by Linford and Chidsey in the early 1990s (Linford & Chidsey, 1993; Linford, 1995) and this type of monolayers has continued to attract attention ever since. Hydrosilylation chemistry requires removal of SiO$_x$, which in most cases is achieved using wet chemistry. On planar silicon surfaces diluted, aqueous HF and NH₄F solutions are used to etch Si(100) and Si(111) substrates, respectively, although a wide variety of etching methods has become available (Zhang, 2001a). This process results in

hydrogen-terminated, oxide-free silicon substrates with Si-H groups. The reaction of H-terminated silicon surfaces with alkenes and alkynes can be performed by making use of high temperatures, UV and visible light irradiation, electrochemistry, hydrosilylation catalysts (e.g., $AlCl_3$), and chemomechanical scribing, as summarized in different reviews (Buriak, 2002; Stutzmann, 2006; Hamers, 2008; Ciampi, 2010).

3.2 Organic monolayers: Si-C versus SiO_x-C

Si-C bonded monolayers have a number of advantages over silane-based monolayers on SiO_x surfaces. First, interface trap densities for Si-C bonded monolayers can be considered remarkably lower than in the case of alkyl chains organic monolayers on naturally oxidized silicon surfaces (Kar, 2001). Also, as already mentioned in §2.1.1.1, silane oligomerization can result in rough layers that are thicker than a monolayer. In contrast, the reaction between a H-terminated Si surface and alkenes or alkynes results in a true monolayer. This is related to the involved zipper mechanism, in which each binding of an alkyl chain directly generates a new radical site on the next-nearest Si surface atom (Linford, 1995). Moreover, the chemical stability of monolayers on SiO_x in aqueous media is poor since the exposure to water pilots the destruction of the monolayer through hydrolysis of Si-O bonds (Calistri-Yeh, 1996). Organic layers formed by hydrosilylation are stable in a number of environments, including air, boiling water, organic solvents, and acids (Linford, 1995).

In the field of SiNW-based devices, the application of Si-C monolayers has a number of other benefits as compared to silane-based surface modifications. First, the removal of SiO_x brings a sensing event (target/analyte interaction) closer to the conducting surface, which increases the sensitivity of the device (Bunimovich, 2006; Zhang, 2008a). Second, the selective functionalization of oxide-free SiNWs is considered to be a supplementary factor that improves the detection sensitivity by avoiding the binding competition between the SiNW and the oxide surface on the rest of the device. Third, several studies show improved electrical properties of Si-C linked monolayers over monolayers on SiO_x, in terms of the flat-band potential and source-drain conductance (Faber, 2005b; Vilan, 2010).

A crucial difference between the silane-based and alkene-based approach becomes clear from, e.g., the preparation of amine-terminated monolayers. While in the case of SiO_x unprotected amines can be used (§2.1.1), e.g., APTES, amine-containing alkenes should be chemically protected as amines can react with H-terminated Si surfaces. The *N*-tert-butoxycarbonyl (t-BOC, Figure 7, alkenes **7a** and **7b**) is a commonly used protecting group for primary amines, but other protecting groups have been used as well (Sieval, 2001a). Apart from amines, also carboxylic acid and alcohol functionalities should be protected before application in the hydrosilylation chemistry (Buriak, 2002).

Characteristic of Si-C bonded monolayers is that the molecular cross-section of the attached alkyl chain prevents reaction of all individual Si–H bonds, i.e., upon formation of a monolayer on Si(111) about 50-55% of the Si–H sites has reacted (Sieval, 2001b), while on Si(100) this is about 30-35% (Sieval, 2000a). The remaining, unreacted Si-H sites are a potential source for the formation of interface states, e.g., via oxidation, which is an unfavourable process in terms of device performance.

3.3 Hydrosilylation on SiNW-based sensor devices

The reported chemistry for functionalizing the oxide-free, H-terminated SiNW sensor devices is limited to one method, i.e., hydrosilylation catalyzed by UV irradiation. This

approach has been applied by different research groups using different etching conditions and probing different types of analytes (Table 3).

The first report on the modification of oxide-free SiNW-based devices is by Heath and coworkers (Bunimovich, 2006). The authors followed an established, multistep protocol (Bunimovich, 2004; Streifer, 2005) that starts with the hydrosilylation of H-terminated SiNWs with tert-butyl allylcarbamate (Figure 7, alkene **7a**) irradiated at 254 nm. After deprotection, the researchers obtained a positively charged amine-terminated monolayer on the SiNWs, enabling the adsorption of negatively charged, oligo ss-DNA.

Surface characterization of the nanowires embedded in a device is a challenge, since conventional analytical tools used for surface characterization require substrates on the micro-scale. For that reason a widely used strategy is to perform the applied chemistry also on planar samples.

Analyte	Receptor	Alkene*	Oxide	Etching Conditions	Reference
ss-DNA	ss-DNA	**7a**	native	2% HF_{aq} (3 s)	(Bunimovich, 2006)
K^+, Na^+	Crown Ether	**7b**	5-10 nm	1% HF_{aq} (50 s) + NH_4F_{aq} (60 s)	(Zhang, 2007)
ss-DNA	ss-PNA	**7b**	~ 5 nm	1% HF_{aq} (50 s) + NH_4F_{aq} (60 s)	(Zhang, 2008a; Zhang, 2008b)
Avidin/ Streptavidin	Biotin	**7b**	not reported	10:1 v/v 40% NH_4F_{aq}/ 49% HF_{aq} (5 s)	(Stern, 2007)
Antigen	Antibody	**7b**			
-	-	**8**, **9**			

Table 3. Overview of the references that report on the chemical modification of the SiNW-based devices via hydrosilylation chemistry.

* The chemical structures of the alkenes are given in Figure 7.

7a: Tert-butyl allylcarbamate (n=1)
7b: 10-*N*-Boc-amino-dec-1-ene (n=8)

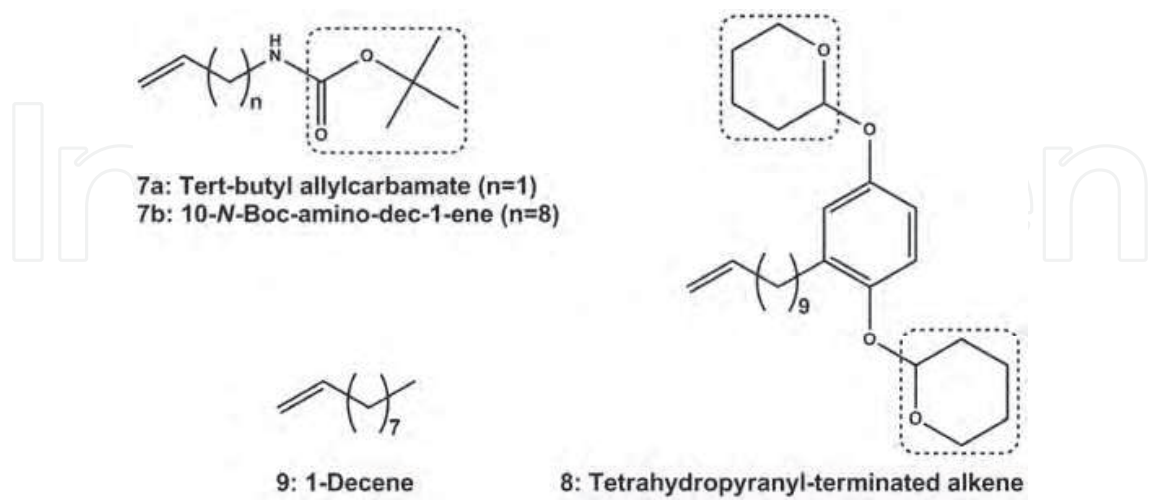9: 1-Decene   8: Tetrahydropyranyl-terminated alkene

Fig. 7. Alkene derivatives that have been chemically bound to oxide-free SiNW sensor devices. The protecting groups on various alkenes are marked in dashed rectangles. For alkene 7a and 7b the protecting group is *N*-tert-butoxycarbonyl (t-BOC), for alkene 8 it is the tetrahydropyranyl (THP) group. See text for further information.

This strategy was also followed by Bunimovich et al. and planar Si(100) samples were analyzed by water contact angle measurements and X-ray Photoelectron Spectroscopy. Moreover, this interesting paper compares Si-C and SiO_x-based monolayers. It is shown that the electrical read-out of oxide-free SiNWs for sensing complementary 16-mer DNA was more profound than on modified, SiO_x-covered SiNWs.

Also Zhang et al. used hydrosilylation chemistry to coat SiNW devices with ss-DNA, although a different strategy was chosen (Zhang, 2008a; Zhang, 2008b). The modification scheme starts with the UV-initiated attachment of 10-N-boc-amino-dec-1-ene (Figure 7, alkene **7b**) to a device with H-terminated SiNWs. After the deprotection of the amino groups the surface was chemically modified with glutaraldehyde, allowing the covalent binding of amino-terminated compounds. Inspired by the work of others on devices with SiO_x nanowires (Strother, 2000; Hahm & Lieber, 2004; Bi, 2008a), they subsequently immobilized PNA. The benefit of this approach over the method reported by Bunimovich et al. is twofold: PNA is not only neutral (see also §2.1.2), it is also bonded covalently. Although multivalent, ionic interactions might be stronger than one single covalent bond, the latter is independent of the salt concentration, making it more robust in wide range of chemically different environments.

As for sample characterization the research group was quite successful in depicting the chemistry performed on the SiNWs. Transmission electron microscopy (TEM) was performed for a morphological study of the non-oxidized SiNW surface. From the TEM data the authors concluded that the surface was nearly uniform, oxide free and did not show visible TEM-detectable defects (Figure 8b). In addition, binding of fluorescently labeled, complementary DNA was used to demonstrate the selectivity of the non-oxidized SiNW surface chemistry and the specificity of PNA-DNA hybridization. Indeed, strong fluorescent signals on the SiNWs were obtained and the bright arrays of SiNWs were clearly visible (Figure 8c).
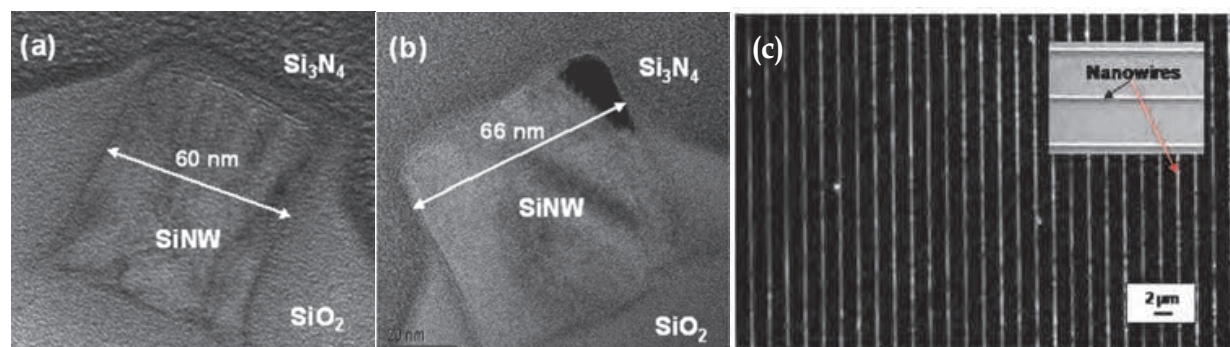

Fig. 8. Cross-sectional TEM micrographs of SiNWs before and after HF and NH_4F etching: (a) SiO_x layer coated on the SiNW surface prior to etching, (b) hydrogen-terminated SiNW after etching, (c) Fluorescent images of Cy3-labeled complementary DNA hybridized to the PNA-functionalized SiNWs. The inset shows SEM micrograph of SiNW arrays. Figure from (Zhang, 2008a) reprinted with permission from Elsevier.

Earlier work by Zhang et al. focused on the sensing of alkali metal ions by the chemical modification of SiNW-based devices with crown ethers (Zhang, 2007). Also in this case alkene **7b** was used, followed by the reaction with glutaraldehyde, resulting in an aldehyde-terminated monolayer. Subsequently, amine-terminated crown ethers were covalently attached. Based on the complexation selectivity of crown ethers to alkali metal ions, the resulting functionalized oxide-free SiNW-based devices could detect Na^+ and K^+.

The sensitivity of protein binding by oxide-free SiNW-based FETs was first reported by Stern et al. using biotin-avidin/streptavidin interactions and antibody-antigen sensing (Aswal, 2006). Three different functionalized alkene derivatives were used in the UV-initiated reaction with H-terminated SiNW devices: 10-*N*-boc-amino-dec-1-ene (**7b**), 2-[2-(undec-10-enyl)-4-(tetrahydro-2H-pyran-2-yloxy)phenoxy] tetrahydro-H-pyran containing a tetrahydropyranyl (THP) protecting group (**8**), and 1-decene (**9**). Only alkene **7b** could be realized for sensing purposes, whereas modification with alkene **8** was ineffective for sensing and alkene **9** aimed as a control. Using alkene **7b**, amino-terminated monolayers were obtained, followed by a common biotinylation protocol using N-hydroxysulfosuccinimide for capturing avidin and streptavidin. For antibody-antigen sensing the capture antibodies were bound to hydrosilylated SiNWs by N-hydroxysulfosuccinimide/ethylene dicarbodiimide coupling chemistry (Hermanson, 2008).

The strategy for protein binding using alkene **8** is different and more complicated, yet very appealing. That is because it creates electrochemically active monolayers on top of the SiNWs. Such electro-active monolayers ensure not only the monolayer formation qualitatively, but they also allow the quantification of the surface coverage. This is based on the fact that the required electrons for the reduction of the electro-active moiety can be measured. The number of electrons is directly proportional to the number of the electro-active groups present and hence to the coverage. As a first step THP-protected alkene **8** was photochemically bound to hydrogen-terminated SiNW. Removal of the protecting THP ethers under mild conditions of 1% toluene sulfonic acid (TSA) in methanol leads to the hydroquinone (Scheme 3). Cyclic voltammetry (CV) in PBS oxidized the hydroquinone to quinone. Finally, they aimed to couple thiolated biotin selectively to the thus formed quinone moieties, but this was not successful, most likely due to the degradation of the device performance that was observed upon chemical modification.
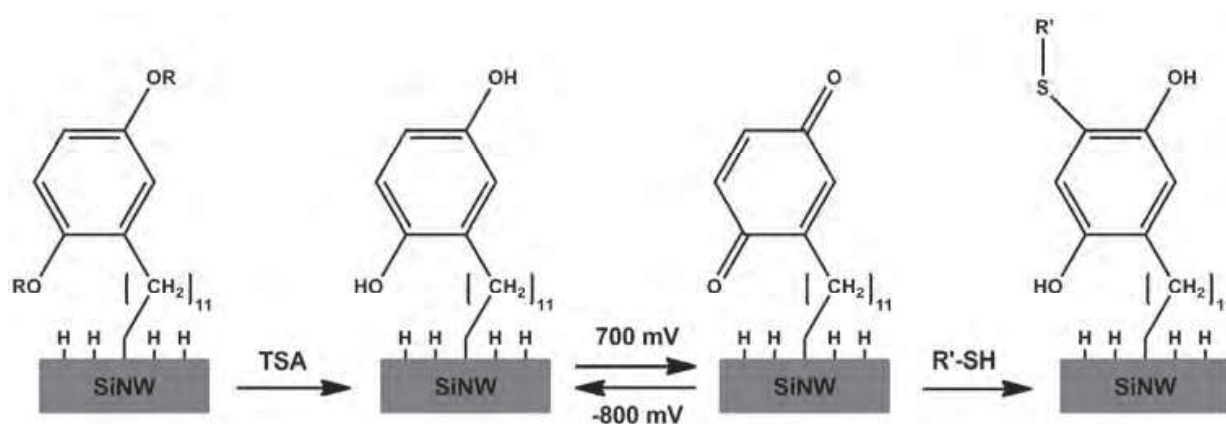
Scheme 3. The strategy reported by the Heath group (Bunimovich, 2004) and also investigated by the Reed group (Stern, 2007) for the selective immobilization of thiolated biotin (R'-SH) via a Michael addition. TSA stands for 1% toluene sulfonic acid. See text for further explanation.

While devices that were modified via UV-induced hydrosilylation using alkenes **7b** and **9** experienced increased leakage currents, the use of compound **8** led to loss of gating behavior, most likely due to the formation of redox-active surface traps. For compound **7b** the authors report a device yield as low as <2% after the deprotection. The work of Stern et al. highlights the importance of validating the device performance after chemical modification.

3.4 Organic monolayers on oxide-free SiNW devices: towards sensing

The observation of changes in device performance upon chemical modification of its sensing area has not only been reported by Stern et al., but also in a few other cases. Yet there is evidence that even non-charged molecules adsorbed on the nanowire alter the device characteristics. Haick et al. showed an improved conductance of the H-terminated SiNWs upon the chlorination/alkylation of the nanowire (Haick, 2006). They reported that methyl-terminated SiNWs exhibit higher source-drain conductance values, lower surface defect levels and higher on-off ratios than oxygenated SiNWs.

Another example of characterizing the surface passivation of a NW prior to sensing is the work of Masood et al. (Masood, 2010). An improved device behavior after hydrosilylation on SiNW with 1-octadecene has been shown by means of capacitance-voltage and current-front-gate voltage electrical measurements. Based on other studies showing that hydrogen-terminated Si(111) surfaces have the lowest reported surface recombination velocity and improved electronic performance as compared to Si(100) surfaces with SiO_2 interfaces, the authors stress the importance of using Si(111) surface to further improve the Si-NW biosensor performance.

4. Concluding remarks and outlook

In order to bind (bio)receptor molecules onto SiNW-based devices, most studies apply the silanization on the nanowire oxide layer. Clearly APTES is the most frequently used silane-based agent, enabling the subsequent immobilization of carboxylic acid- or aldehyde-terminated biomolecules. More often, further derativization with glutaraldehyde has been applied to chemically bind amine-terminated biomolecules. A disadvantage of silane compounds is their ability to react with each other via cross-linking of the alkoxy units, resulting in rough, unordered multilayers. Based on the optimization studies on planar silica substrates that have become available (Howarter & Youngblood, 2006) and reports on the quality differences between vapour- and wet chemistry-prepared APTES layers (Fiorilli, 2008), there is room for the improvement of silane chemistry on SiNW-based devices. Phosphonate monolayers are an interesting alternative for silane-based monolayers, due to their higher hydrolytical stability and the less critical pretreatment of the oxide surface that is required.

Apart from covalent functionalization of SiNW-based sensor devices also physisorption has been studied, which enabled the detection of several compounds and ions. Covalent attachment of (bio)molecules to sensor surfaces may be appealing in terms of device stability, but some systems, e.g., membrane receptors require a more dynamic environment. It has been shown that a phospholipid monolayer can be covalently immobilized on SiO_x (Heysel, 1995) and Si-H (Charrier, 2010) surfaces, enabling the non-covalent immobilization of a second phospholipid layer. However, this strategy may hamper the fluidic properties of the bilayer, which is vital for the incorporation of biologically active structures into the membrane. The fusion of spherical unilamellar vesicles onto surfaces overcomes this problem. So far, only two different transmembrane ion channels on SiNW-based devices have been reported (Misra, 2009), but lipid bilayers provide a matrix for a virtually unlimited number of transmembrane proteins that can accommodate different functionalities.

Physisorbed PE layers are not covalently attached; nevertheless they are very stable, due to the multivalent character of the interaction. The multivalency is also beneficial

regarding the detection of a PEs that adsorbs onto the SiNW-based device. LbL films of PE have been employed for various applications, including electrochemical sensing and biosensing and they have also contributed to the investigation of fundamental studies in electrochemistry (Crespilho, 2006). The work of Ingebrandt and coworkers (Vu, 2010) can now be extended to the use of biologically relevant PEs and perhaps also the incorporation of nanoparticles.

An interesting candidate to replace SiO_x layers on silicon surfaces is found in alkene-prepared organic monolayers. There are a number of benefits for monolayers on oxide-free silicon over silane-based layers: a) no risk of oligomerization, resulting in a true monolayer, b) higher chemical stability, c) selective functionalization, i.e., the background surface is not functionalized, and d) a lower density of interface traps. Although a wide variety of preparation procedures for hydrosilylation surface chemistry are available, so far only UV-initiated methods have been used in the chemical modification of oxide-free H-terminated SiNW devices. This can be explained by the fact that the research in this direction is still in its early days, and it probably will not take long before some of the other available preparation methods will be explored on SiNW-based devices. An important issue in this regard is the surface orientation of the nanowire (Bunimovich, 2004). In addition, a very good monolayer quality is needed, reducing the number of interfacial defects (Seitz, 2006). In contrast to SiO_x-covered SiNW-based devices, the insulating properties in the case of oxide-free SiNW-based devices are exclusively to be realized by the organic monolayer itself. One possibility to improve the monolayer quality is by using alkynes instead of alkenes (Sieval, 2000b; Faber, 2005a; Scheres, 2010).

To conclude, selective functionalization of the nanowires is critical to retain sensitivity as the modification of the background oxide results in a reduced sensitivity. In addition, the modification of individual nanowires that are part of a larger array is essential to perform a multi-analysis using a single device. Continued advances in the preparation of well-defined, defect-free, organic-semiconductor interfaces will further improve the performance of SiNW-based devices. The combination of an increasingly growing number of interesting (bio)receptors, sophisticated device fabrication methods, improved electrical characterization procedures and advanced organic surface modification does not only provide unlimited research opportunities, it will also contribute significantly to diverse, highly usable sensor applications in a variety of fields.

5. Acknowledgment

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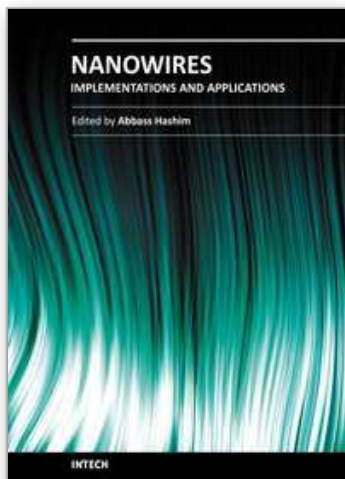
Nanowires - Implementations and Applications

Edited by Dr. Abbass Hashim

This potentially unique work offers various approaches on the implementation of nanowires. As it is widely known, nanotechnology presents the control of matter at the nanoscale and nanodimensions within few nanometers, whereas this exclusive phenomenon enables us to determine novel applications. This book presents an overview of recent and current nanowire application and implementation research worldwide. We examine methods of nanowire synthesis, types of materials used, and applications associated with nanowire research. Wide surveys of global activities in nanowire research are presented, as well.

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