

Dual-gated field effect transistors for sensing applications

Master thesis

Mathias Wipf mathias.wipf@stud.unibas.ch

March, 2010

Submitted to Prof. Christian Schönenberger University of Basel Department of Physics

Contents

1.	Intro	oduction	1						
	1.1.	Conductance of a semiconducting nanowire	2						
	1.2.	Field effect sensors	4						
	1.3.	Nernst equation	4						
2.	Sam	ple fabrication and measurement methods	7						
	2.1.	Device fabrication	7						
		2.1.1. Wire lithography	7						
		2.1.2. Aluminum oxide atomic layer deposition	9						
		2.1.3. Liquid channel and sealing	10						
	2.2.	Measurement setups	10						
		2.2.1. FET characterization	11						
		2.2.2. Gate space mapping for measurements in liquid	11						
		2.2.3. Leakage current measurements	12						
3.	Nan	owire FET characterization in air	13						
-	3.1.	Nanowire FET dependence on back-gate voltage	13						
	3.2.	ALD shift	13						
л	C		17						
4.	Jup	Lookage current in liquid environment	17						
	4.2.		19						
5.	Tran	sport measurements in pH buffer solutions	25						
	5.1.	pH sensitivity in the accumulation regime	25						
	5.2.	Measurements in the inversion regime	27						
	5.3.	pH measurements with APTES coated surface	27						
6.	Inter	rpretation of high sensitivity beyond the Nernst limit	31						
7.	Sum	mary and conclusion	35						
Α.	App	endix	43						
	A.1.	Fabrication	43						
		A.1.1. UV lithography	43						
		A.1.2. Metal evaporation	43						
		A.1.3. Etching	44						
		A 1.4 Atomic layer deposition	44						
		A 1.5 Liquid channel	45						
		A 1 6 Bonding	46						
		A 1 7 Epoxy sealing	46						
	Α2	Functionalization with APTES	46						
	A 3	Produced samples	46						
	,		10						

1. Introduction

The use of molecular sensors in biology and medicine has become essential. Detection of specific molecules such as DNA or proteins is getting more and more important for research. Many different detection techniques for chemical and biological molecules exist on the market. Most of them work with slow and expensive methods, such as fluorescence or cantilever detection [1, 2]. At present, huge effort is made to develop fast response, cheap and ultrahigh sensitive sensors. A promising approach is the use of silicon based sensors, since the production of silicon devices is well established and very low cost is predictable [3]. Field effect transistors (FET) are capable to convert a change in potential into an electronic response. The idea of gating a ion-sensitive field effect transistor (ISFET) using the electrostatic potential of adsorbed molecules has been introduced in the 1970s [4] and has gained a large research community [5, 6]. Technological progress made it possible to fabricate carbon nanotube (CNT) FETs [7–9] and nanowire (NW) FETs [10–12] from which high sensitivity can be expected due to their high surface to volume ratio. For detecting biomolecules like proteins or DNA in biological solutions, very high sensitivity, meaning detection of substances with concentrations down to femto-molar range [12] is needed.

Downscaling allows the integration of large numbers of sensors on a chip. Highly integrated sensors offer simultaneous tests and differential measurements at high response time. The idea of point-of-care diagnostics in future healthcare is a further driving force for smaller and faster sensing units. The application possibilities reach from medical, biological and pharmaceutical use to detectors of harmful substances in food and environment. This large field of everyday-use possibilities promises a huge business volume. For commercial applications reproducible and stable devices are needed. Today's science in this field is focused on understanding the basic mechanisms of field effect sensors [13–15]. Various different approaches are promising. Bottom-up techniques with the use of CNTs and growth of nanowires have the advantage of extremely high surface to volume ratio, but the lack of very poor reproducibility. Top down methods as silicon wafer lithography are well understood and are feasible for mass production which makes them more attractive for application use.

Design and fabrication of electronic biosensors based on FET devices require understanding of interactions between semiconductor surfaces and organic biomolecules [15]. In biology and pharmaceutical research a lot of work has been done in designing receptors for specific targets. Such receptors could functionalize the FET surface. The interaction with their specific analytes is ought to change the FET's conductance. However, such functionalized sensors require reliable design and fabrication of ISFET devices, because immobilized target molecules are located at least a few nanometers above the semiconductor surfaces and are surrounded by counterions in the analyte solution. Adding the diffusion of target analytes makes high demands on the sensitivity.

Detecting small concentrations down to the femto-molar range requires high sensitivity, which means a high electrical response at small electrostatic changes at the device surface. A promising tool to investigate sensing properties quantitatively, is the detection of pH changes. The induced surface potential shift due to protonation and deprotonation of the surface hydroxyl groups can be described by the Nernst equation, which predicts a maximum electrical shift of $\approx 60 \,\text{mV/pH}$ at room temperature [13].

At present a lot of research is done in this field. In the project I have worked on, a dualgated device was developed. The focus of our team during my thesis was to design reproducible pH sensing devices based on silicon nanowire field effect transistors (SiNWFET). A reliable lithography process had been established in previous work [16–18]. A remaining challenge was to overcome leakage current in liquid environment, which is a common problem in such devices [19, 20]. Protons from the solution are able to penetrate silicon oxide layers. This leads to currents in the range of $10^{-8} - 10^{-6}$ A at a potential difference of a few volts over the oxide layer. With gate voltages in the working range of $\approx -7 - 5$ V the leakage current is in the same range as the current through the wire. With such a high leakage ratio the signal current becomes too small and sensing is not possible. An atomic layer deposition (ALD) process was the solution to reduce the leakage current and enhance pH sensitivity. My main focus was to determine the influence of the ALD layer on transport characteristics and leakage current.

1.1. Conductance of a semiconducting nanowire

The main advantage of FET based sensors is their ability to transduce charges into electrical signals, which makes them fast and cheap to read out. The change in conductance of a semiconducting nanowire is the basic output of an ISFET. The conductance can be calculated starting from Ohm's law.

$$J = \sigma_{con}(r)E \tag{1.1}$$

where J is the current density, σ_{con} is the conductivity and E is the electric field pointing along a cylindric nanowire with radius r [21]. The conductance $G = I/V_{SD}$ can be found by integrating the current density over the nanowire cross section area:

$$I = \int_{A} J(r) \cdot dA \tag{1.2}$$

$$= \int_{A} \sigma_{con}(r) \cdot E \cdot dA \tag{1.3}$$

$$= \int_{A} \sigma_{con}(r) \cdot \frac{V_{SD}}{L} \cdot dA \tag{1.4}$$

where I is the current, V_{SD} the applied voltage along the nanowire and L the nanowire length. The conductivity can be written as the sum of the electron mobility, $\mu_n(n_0, r)$ times the

The conductivity can be written as the sum of the electron mobility, $\mu_n(n_0, r)$ times the electron concentration, n(r) and the hole mobility, $\mu_p(p_0, r)$ times the hole concentration, p(r). The conductance can therefore be written as

$$G = \frac{1}{L} \int_{A} \sigma_{con}(r) \cdot dA \tag{1.5}$$

$$= \frac{1}{L} \int_{A} e \cdot [\mu_{n}(n_{0}, r) \cdot n(r) + \mu_{p}(p_{0}, r) \cdot p(r)] \cdot dA$$
(1.6)

The mobilities depend on the doping of the semiconductor. The electron and hole concentration can be described by Boltzmann statistics.

$$n(r) = n_0 \cdot exp\left(\frac{-e\Psi_1(r)}{k_BT}\right)$$
(1.7)

$$p(r) = p_0 \cdot exp\left(\frac{e\Psi_1(r)}{k_BT}\right)$$
(1.8)

where k_B is the Boltzmann constant, T the temperature in Kelvin and Ψ_1 the potential inside the nanowire. n_0 and p_0 are constants for electron and hole concentrations and are related as follows

$$n_0 \cdot p_0 = n_i^2 \tag{1.9}$$

where n_i is the intrinsic charge carrier concentration.

To calculate the conductance only the potential inside the wire (Ψ_1) has to be known [21]. But since Ψ_1 is influenced by a complex system with different interfaces, the surrounding potentials and their coupling to the nanowire are the point of interest.

In the case of a dual-gated FET, a back-gate, a liquid gate and charges at the sensing surface define Ψ_1 . Each gate couples differently to the nanowire depending on the gate oxide capacitance. A model of the capacitances and the relating gate couplings in our system is given in chapter 6. In general, the influence of a gate on I_{SD} can be siplified by regarding a rectangular nanowire with width w, height h and length L in the accumulation regime with majority charge carrier n. The source-drain current I_{SD} can be written as follows [18].

$$I_{SD} = \frac{w \cdot h}{L} \cdot V_{SD} \cdot \mu \cdot n \cdot e \tag{1.10}$$

which is valid for small V_{SD} , meaning the linear regime.

Adding a gate to the system, its potential (gate voltage, V_G) and gate oxide capacitance (C_{gate}) have to be taken into account. The charge $n \cdot e$ can be described as in a capacitor model

$$n \cdot e = \frac{C_{gate}}{vol_{NW}} \cdot (V_G - V_{th}) \tag{1.11}$$

where V_{th} is the threshold voltage and vol_{NW} is the nanowire volume [22]. Defining a capacitance per wire area $C'_{gate} = C_{gate}/wL$ gives a final equation for the source drain current, depending on the gate voltage:

$$I_{SD} = \frac{w}{L} \cdot V_{SD} \cdot \mu \cdot C'_{gate} \cdot (V_G - V_{th})$$
(1.12)

A p-doped semiconductor, as it was used in our case, can be driven in accumulation by applying a negative gate voltage. Thereby, the energy valence band edge E_V bends upwards and E_V is closer to the Fermi level E_F . The charge carrier density depends on the energy difference E_F-E_V and is therefore increased at the surface. Accumulation of majority charge carriers (holes) caused by this energy band bending leads to an increased conductance. The gate voltage where the transistor is turned "on", is called threshold voltage (V_{th}). We defined it as the zero crossing of the linear fit as shown in section 3.1. Ideally, there is no current flowing below the threshold voltage. In fact, there is a so-called subthreshold regime, where the current is small and varies exponentially with the gate voltage. The subthreshold swing describes the back-gate voltage per decade in conductance. Above the threshold voltage, the current increases proportionally with the gate voltage (if $V_{SD} < V_G$) [17]. This linear regime becomes nonlinear and saturates at a certain gate voltage.

More positive gate voltage bends E_V downwards which reduces the number of charge carriers. The device is in depletion when the charge concentration goes to zero until no current flows. Increasing the gate voltage further to the positive side causes an accumulation of minority charge carriers (electrons) at the gate oxide and creates a conductive channel from source to drain, called inversion.

The doping in our case was rather low (boron p-doped, 10^{15} - 10^{16} cm⁻³) which lead to an ambipolar behavior, where the inversion region already occurred at low gate voltage (~ $1V_{BG}$, see fig. 3.1).

1.2. Field effect sensors

Field effect sensors can be based on FETs and work on the principle of detecting shifts in localized electric potentials. This shift can be induced due to chemical interactions at the device surface causing a local charge accumulation or a change in the charge polarization. A change in the electric field at the device surface acts as a gate on the nanowire and changes its potential. The charge carrier density is influenced by this field-effect, thus leading to accumulation, depletion or inversion of the semiconductor's conduction channel. In ion sensing there is a maximum possible threshold voltage shift for field effect sensors, which can be estimated with the Nernst equation.

In our case, the ion sensitive FET (ISFET) is a dual-gated structure with the device layer enclosed by the top-gate insulator (top oxide, TOX) and the back-gate insulator (buried oxide, BOX). Therefore, the device has two interfaces which interact with the individually controllable back-gate and top-gate (liquid gate). The threshold voltage shifts proportional to charges depending on all the capacitances of the two gates (C_{tot}).

Adding a positive charge Q to the top oxide decreases the threshold voltage of accumulation related to the back-gate according to

$$\Delta V_{th} \sim -\Delta Q/C_{tot} \tag{1.13}$$

where ΔQ is the net charge added at the top oxide [23].

In an ISFET, ions close to the surface change the gate potential and thus the threshold voltage. Changes in ion concentration, such as pH value, can be measured by an ion-sensitive barrier on the top oxide. In the case of a pH sensitive device, a layer out of SiO_2 , Si_3N_4 or Al_2O_3 acts as ion-sensitive barrier, since the hydrolyzation of OH groups adsorbs charges to the top oxide. In fig. 1.1 a sketch shows how pH change has an influence on the gate's potential. For more complex and specific molecule detection, the device must be functionalized with a coordinated linker.

lons in aqueous solutions are surrounded by the polar water molecules. This aggregation shields their electrostatic potential. If ions are accumulated at a surface due to electrostatic interaction or specific binding, they still aggregate water molecules and counterions. Hence their electric field is shielded. The Debye length λ_D describes the length over which mobile charge carriers screen out electric fields and is given by

$$\lambda_D = \sqrt{\frac{k\,\mathcal{T}\epsilon_r\epsilon_0}{2\,N_A e^2\,l}}\tag{1.14}$$

where N_A is the Avogadro number and ϵ_R is the permittivity of the electrolyte (water). The ionic strength *I* of a solution is defined as the sum of the squared charge *Z* times the concentration *c* of all ionic species in the solution: $I = \frac{1}{2} \sum_i z_i^2 C_i$. For a 100 mM NaCl solution, λ_D would be \approx 7 nm. A layer of accumulated charges at a surface is called Gouy-Chapman double layer. The so-called double layer capacitance (C_{dI}) is given by [24]

$$C_{dl} \approx \frac{\epsilon_r \epsilon_0}{\lambda_D} \tag{1.15}$$

1.3. Nernst equation

In the case of pH measurements, the potential shift at the device surface can be described with the Nernst equation. The mechanism responsible for the oxide surface charge can be described

4



Figure 1.1.: Sketch of the surface oxide. In our case Al_2O_3 was used as top oxide. At neutral pH, the hydroxyl groups stay uncharged. Decreasing the electrolytes pH protonates the hydroxyl groups $(-OH_2^+)$ which act as local positive gate on the SiNWFET. At high pH the hydroxyl groups get deprotonated $(-O^-)$ and act as a local negative gate.

by the equilibrium between the so-called amphoteric surface hydroxyl sites and the H^+ -ions in the solution. The reactions for an aluminum oxide surface are

$$AI - OH \Leftrightarrow AI - O^- + H_B^+ \tag{1.16}$$

$$AI - OH_2^+ \Leftrightarrow AI - OH + H_B^+ \tag{1.17}$$

with H_B^+ representing the protons in the bulk solution. The difference between the oxide surface potential and the bulk solution is $\psi_0 = \psi_S - \psi_B$. With ψ_0 and the Boltzmann equation, the activity of the bulk protons $a_{H_B^+}$ can be related to the activity of the protons in the direct vicinity of the oxide surface, $a_{H_c^+}$ [6].

$$a_{H_S^+} = a_{H_B^+} \cdot exp\left(\frac{-q\psi_0}{kT}\right) \text{ or } (pH_S - pH_B) = \frac{q\psi_0}{kT}$$
(1.18)

The effect of a small change in the surface pH (pH_S) on the change in the surface potential ψ_0 can be written as follows:

$$\frac{\partial \psi_0}{\partial \rho H_S} = \frac{\partial \psi_0}{\partial \sigma_0} \cdot \frac{\partial \sigma_0}{\partial \rho H_S} = \frac{-q\beta_{int}}{C_{dif}}$$
(1.19)

where σ_0 is the surface charge density. The ability of the double layer to store charge in response to a small change in the potential $\partial \sigma_0 / \partial \psi_0$ is defined as the differential double-layer capacitance C_{dif} . Combining eq. 1.19 and 1.18 results in the general expression for ISFET pH sensitivity:

$$\frac{\partial \psi_0}{\partial \rho H_B} = -2.3 \frac{kT}{q} \cdot \alpha \text{ with } \alpha = \frac{1}{\frac{2.3kT \cdot C_{dif}}{q^2 \beta_{ext}} + 1}$$
(1.20)

The parameter α is a dimensionless sensitivity parameter that varies between 0 and 1, depending on the intrinsic buffer capacity β_{int} of the oxide surface. In the ideal case, α is equal to 1 which results in a sensitivity of 59.2 mV/pH at a temperature of 298 K. This number is the so-called Nernst limit. β_{int} is not very high for SiO₂. pH-sensitivities around 30 – 40 mV/pH were achieved so far [13, 25]. Better results were achieved using different layers as Si₃N₄, Ta₂O₅ and Al₂O₃ which seem to have higher buffer capacities [26, 27].

In our case, Al_2O_3 was used. The sensitivities we obtained were surprisingly high and beyond the Nernst limit, which on one hand can be attributed partially to the Al_2O_3 layer [26], but for the most part referred to the dual gate measurements where not only C_{dif} is taken into account. A more detailed explanation is given in chapter 6.

5

2. Sample fabrication and measurement methods

2.1. Device fabrication

The sensing devices were produced with standard UV lithography techniques. A silicon on insulator (SOI) wafer from *SIMGUI* was used. The silicon had a <100> orientation and was p-doped with $\approx 10^{15}$ boron atoms per cm³ (10 - 20 Ω cm). The ion implanted buried oxide (BOX) layer had a thickness of 155.1 nm. The device layer had an original thickness of 150 nm and was oxidized thermally by the *PSI* to a final thickness of 80 nm. The resulting top oxide layer had a thickness of 40 nm. A wafer cross-section for each production step is shown in fig. 2.1.

The devices were fabricated in batches of ca. 8 samples with four wires each. Figure 2.2 shows an overview illustration of the wire processing and the pattern of one sample. The size of a sample is $\approx 2 \times 2 \text{ mm}^2$. The wires dimension is $1.4 \times 10 \,\mu\text{m}^2$ at a thickness of 80 nm (given by the device layer).

The wafer was cut to batch size along the <100> and <010> direction and cleaned in acetone, isopropyl alcohol (IPA) and UV-ozone (UVO) before processing.

2.1.1. Wire lithography

The cleaned wafer was coated with hexamethyldisilazane (HDMS) which acts as a adhesion layer for photoresists. The wafer was spin-coated with negative UV-photoresist *ma-N* 415 (*Micro resist technology*) and prebaked for 90s at 91.5°C. The photoresist was UV exposed through a chromium mask and developed using *ma-D* 332 S.

The sample was then coated with 60 nm thick chromium evaporation. In a lift-off process the photoresist and the Cr on top of it were removed (see fig. 2.1b).

The remaining Cr was used as a mask for plasma silicon oxide etching (CHF₃ plasma), as seen in fig. 2.1c. Afterwards, the chromium was removed with a potassium permanganate (KMnO₄) base etch process.

The remaining top oxide layer acted as a mask for the silicon etching process (see fig. 2.1d). First, the native oxide on the silicon layer was removed in hydrofluoric acid (HF) buffer solution. Afterwards, the silicon was etched anisotropic in 25% tetramethylammonium hydroxide (TMAH) at 45°C. TMAH etches the <110> direction of the silicon crystal, while the <111> direction is barely affected. The resulting width of the wires was around $0.8 - 1 \,\mu$ m with freestanding <111> orientated side walls [18].

In a second lithography step the sample was protected with photoresist, leaving the contact leads open. The silicon oxide on top of the contacts was etched in buffered HF, before a 100 nm aluminum layer was evaporated. Removing the photoresist in acetone, led to aluminum coated contact leads. Annealing the contacts for 10 min at 450°C in forming gas to achieve a better electrical interface between silicon and aluminum, due to contact barrier minimization and aluminum diffusion (see fig. 2.1f) [18].



Figure 2.1.: SOI-wafer profile during the sample fabrication process. a) Oxidized SOI-wafer b) Chromium mask evaporation c) Top SiO₂ etching d) Cr and silicon etching e) Top SiO₂ etching for contacts f) Al contact evaporation and annealing g) Al₂O₃ ALD h) Az resist as liquid channel.



Figure 2.2.: a)Shows the UV mask patterns. Green: Device structure. Yellow: Al contacts. Grey: Liquid channel (colored area is not covered with Az resist). Each sample has four wires (indicated in black) with a width of 1.4 μ m and a length of 10 μ m. The sample size with contact leads is $\approx 2 \times 2$ mm. b) Shows the sample fabrication overview up to Al contacts. Illustration of one wire which is not related to the sample pattern and is not to scale. The figure is adapted from [17].

2.1.2. Aluminum oxide atomic layer deposition

To prevent ions from leaking through the device and the BOX layer when measuring in liquid, the samples were covered with Al_2O_3 by atomic layer deposition (ALD) with a Savannah ALD System, (Cambridge NanoTech Inc). During ALD, a very dense film is grown atom by atom all over the substrate (see fig. 2.1g).

Before the ALD process, the samples were dipped in buffered HF to remove the native oxide on the silicon surface. In the reaction chamber the sample was heated to 225°C under constant N₂ flow. The hydroxylated silicon and silicon oxide surface reacted with the precursor gas Trimethylaluminium (TMA). Since TMA does not react with itself, the surface was passivated by the formed monolayer. In a next step, the unreacted TMA was pumped out and the chamber was floated with highly pure water. H₂O removed CH₃ by creating Al-O-Al bridges and passivated the surface with Al-OH bonds. CH₃ and H₂O reacted to CH₄ and were pumped out of the chamber. These steps formed a cycle and could be repeated in any number. The thickness of the resulting Al₂O₃ layer was between 5 and 44 nm, depending on the number of ALD cycles (100 cycles $\approx 11 \text{ nm}$) [28].

ALD has several advantages [29]:

- The layer thickness is dependent only on the number of deposition cycles.
- No need of reactant flux homogeneity.
- No gas phase reactions.
- Atomic level control of material composition.
- High quality materials with high dielectric strength, low pinhole density and uniformity over large area substrates are obtained at low temperature.

The extremely dense resulting film covers also pinholes in silicon oxide which are thought to let protons pass and cause leakage current.

2.1.3. Liquid channel and sealing

To prevent leakage current and contact of the liquid with the aluminum, the area in touch with liquid needed to be reduced. Therefore the sample was covered with negative photoresist AZ 826 MIF from AZ electronic materials. With a last lithography step, a very small liquid channel (8 μ m wide opening) perpendicular to the four wires was defined (see fig. 2.3a and 2.1h). The remaining photoresist was hardened with UV light.

The sample was cut out of the batch and glued in a chip carrier with silver conductive paste. Afterwards, the contacts as well as the substrate Si layer, which acts as back-gate, were bonded to the chip carrier pins.

As a last step, the chip carrier was sealed with epoxy (*EPO-TEK 302-3M 80Z, Polyscience AG*), leaving the liquid channel open (see fig. 2.3b).

Two batches were produced during my master thesis. Batch *S* was used to reproduce previous results and to produce samples for functionalization. Batch *A* was to test the influence of Al_2O_3 ALD on electrical and leakage properties. More details to the fabrication protocol are given in appendix A.1.



Figure 2.3.: a) Image of a sample with four SiNWFET. To reduce leakage current only a small area around the wire is exposed to liquid (blue area), the rest of the sample is covered with AZ resist. Additional sealing with epoxy is used to cover the bonds and contact areas. b) Illustration of a wire. Epoxy covers all contacts, but the wire

2.2. Measurement setups

Different measurement setups were used to characterize the samples in air and in liquid. Most of the measurements were taken with a *SR 830 DSP* lock-in amplifier from *Stanford research systems* and a *Keithley 2000 multimeter*. Some DC air measurements were taken with a *Keithley 2636A source meter*. The devices showed the same behavior in air whether measured with AC or DC bias. All measurements were performed at standard conditions (Room temperature and atmospheric pressure).

2.2.1. FET characterization

The transistor characteristics were measured in air. The bias voltage (V_{SD}) was either 10 mV or 100 mV. The back-gate voltage (V_{BG}) was swept from -10 V to 10 V back and forth. AC voltage was applied at a frequency of 317 Hz. Sketches of the measurement setups are shown in fig. 2.4. Threshold voltages were calculated by linear fits of the linear regions.

10



Figure 2.4.: a) AC measurement setup. Bias voltage and current readout was done done with a lock-in. b) DC measurement setup, measured with the Keithley source meter. Figures are adapted from [30].

2.2.2. Gate space mapping for measurements in liquid

The liquid cell shown in fig. 2.5 allowed to change the solution, included a platinum electrode to apply a voltage (V_{Ig}) and was designed to insert an electrode to measure the liquid's potential (V_{ref}) . The liquid measurement was similar to the air measurement (see fig. 2.5b). A 100 mV bias (at 317 Hz) was applied over the wire. The liquid gate was swept, so that the liquids potential was between -1V and 1V, while the back gate was changed stepwise. Plotting the conductance as a function of back-gate and liquid potential, the conductance maps for every pH could be compared. pH reference solutions (*MERCK Titrisol buffer solution*) from pH 4 up to pH 12 were used. The measurements for ion sensitivity were done the same way by taking deionized water and solutions of different KCl or NaCl ion concentrations.



Figure 2.5.: a) Illustration of the liquid cell [17]. The sample is fixed in a chip carrier, bonded and sealed with epoxy. In the liquid cell the solution can be changed and via a Pt-electrode its potential can be shifted (liquid-gate, V_{Ig}). Additionally a reference electrode can be built in, to control the potential of the liquid (V_{ref}). b) pH measurements. V_{bg} is applied from the back of the device while the liquid gate V_{Ig} is applied via a Pt-electrode immersed in the solution. The liquid potential V_{ref} is measured by a calomel reference electrode. Bias voltage V_{SD} through the wire and current readout is done by a lock-in amplifier. Figure is adapted from [30].

2.2.3. Leakage current measurements

Leakage current occurs due to ion movement through the silicon and silicon oxide (BOX layer). To measure the leakage current, the liquid-gate voltage was swept and the current was measured at the back-gate and the wire contact, respectively (see fig. 2.6). A *I* to *V* converter with an amplification factor from -10^5 up to -10^8 was used.



Figure 2.6.: Leakage measurements. To measure the leakage current through the device and BOX-layer, voltage was applied at the liquid and current was measured with a I-V converter at the back-gate (a) resp. at the wire (b). In (b) the second wire contact is left floating. Figures are adapted from [30].

3. Nanowire FET characterization in air

To use silicon nanowire FET as sensing devices, their electrical transport response on the backgate voltage needs to be understood. As seen in formula 1.12, the current through the wire depends on the source drain voltage, the back-gate voltage and the device properties as oxide capacitance and device geometry. In an ambipolar FET three different transport regimes exist. Depending on the back-gate, the semiconductor surface can be in accumulation, depletion or inversion. In our devices, the silicon substrate was used as back-gate. Therefore the back-gate affected the whole device including the contact leads.

3.1. Nanowire FET dependence on back-gate voltage

Air measurements as seen in fig. 3.1 show that the reproducibility of the nanowires was very good. Nearly all the working wires show very low hysteresis and ambipolar characteristics. Due to the p-doped semiconductor, accumulation is seen at negative V_{BG} . The threshold voltage (V_{th}) at the accumulation region is around -5 V and at the inversion region around 0 V, but varies a little for each wire. The subthreshold swing, indicated in fig. 5.1(b) is around 300 mV/dec. Batch A showed higher diversity in electrical properties, coming from problems during the production. The wires showed a very rough surface.



Figure 3.1.: Conductance G versus back-gate V_{BG} for four different wires on sample a5 from batch A (a) and s5 from batch S (b) before ALD. Very small hysteresis is visible. The threshold of the different wires align very well for batch S, but show variations for batch A, which corresponds to the poor shape of the wires. Threshold values V_{th} are extracted with a linear fit (dashed line, fig a) of the linear transconductance section. b) Left axis for linear scale, right axis (Δ) for logarithmic scale. Dashed line shows the subthreshold swing S which is 300 mV/dec for wire 1.

3.2. ALD shift

Depositing an aluminum oxide layer on top of the device changes the silicon properties at the interface and hence changes the conductance channel characteristics. As seen in fig. 3.2 which

shows the conductance of a wire before and after ALD, Al_2O_3 shifts the conductance curve to the right, meaning the threshold voltage is less negative. At the same time the slope of the linear region (transconductance) becomes steeper. V_{th} is shifted by $\approx 1V$. This shift is not consistent for all the wires, but seems to increase with increasing numbers of ALD cycles.



Figure 3.2.: Sample a4w1 air measurements before and after ALD. The Al_2O_3 on the surface changes the FET properties. On the one hand, with ALD, the p-site threshold is shifted to the right. On the other hand, the slope is getting steeper (indicated with blue arrows). Additionally a kink occurs above the linear region on the p-site.

The samples from batch A were coated with different Al_2O_3 thicknesses. In fig. 3.3 the mean change in V_{th} and slope for each sample is plotted versus number of ALD cycles. The deviation of the shifts for the different wires is very large, which is attributed to the bad wire quality. Nevertheless a slight trend to a larger threshold shift with increasing ALD cycles can be seen. Shifts by more than 1 V were found, resulting in V_{th} around -4V. Also a small trend to a steeper transconductance is visible.

The threshold shift can be explained by an additional p-doping effect of the aluminum [31]. Due to this doping effect, less negative gate voltage is needed to reach accumulation. The slope change can be explained by considering the total capacitance. Adding an additional layer on top increases the total capacitance of the device. Since the transconductance is directly proportional to the capacitance ($|\partial G/\partial V| \sim C_{tot}$) [17], the added capacitance led to steeper slopes in the accumulation regime. With ALD a kink in the accumulation transconductance appears. It's origin is at present not quite clear but is thought to come from conductance saturation. Since liquid measurements were performed in a range of lower back-gate voltage, this effect did not affect the results. Increasing the number of ALD cycles further would probably emphasize the change of the transconductance and V_{th}, but was no use for the basic idea of ALD, which is reducing the leakage current by closing the pinholes of silicon oxide.



Figure 3.3.: a) Mean threshold shift of batch A. Due to the bad quality of this batch, the standard deviation is quite large. There seems to be a tendency to larger shifts with increasing Al₂O₃ thickness, which is assumed to occur from a p-doping effect of the aluminum. The data at 120 ALD cycles is the mean value of the different batch S samples. Data at 400 ALD cycles responds to a single wire of a previous produced sample. b) Mean slope change of batch a. A slight trend to steeper slopes (more negative) with increasing Al₂O₃ thickness is visible. The oxide layer increases the total capacitance of the system and therefore increases the transconductance. The blue numbers indicate the number of wires included in the data point.

4. Support measurements in liquid

To use a SiNWFET as a biosensor, it needs to be sensitive to charged particles in a solution such as DNA or proteins. The sensor should respond to a change in surface potential by a change in conductance. Measuring in liquid implicates leakage current and multiple effects at the sensor interface. Different types of ions interact differently with the surface. Surface effects of silicon and silicon dioxide are well known, but less established for Al_2O_3 . For selective detection of ions in a biological solution, basic interactions of ions need to be analyzed.

To measure the electrical response on charge carriers in a solution, the wires conductance was measured in different electrolytes. Samples with Al_2O_3 protection layers of different thicknesses were compared to investigate the leakage current.

Measurements at different ion concentrations were made to make sure that charges on the sample surface can be detected. For a quantitative approach and sensitivity analysis, series of pH buffer solutions were measured.

Many samples could not be used for liquid measurements, due to problems during the sample production. Problems during bonding and epoxy sealing damaged several samples. Batch A showed an extremely weak conductance response on the liquid gate in the accumulation regime. It is assumed that the aluminum contacts were not well aligned to the wires and therefore the contact resistance was large in all the batch A samples. This is the reason why many measurements were performed in the inversion regime, although the response is not very stable in this region. An overview of the produced and measured samples is given in appendix A.3.

4.1. Leakage current in liquid environment

Although the area exposed to the liquid is reduced to a minimum, leakage current from the liquid into the device and vice versa is too high without using a protection layer. Fig. 4.1a shows that in the case of an untreated SOI-wafer with an area of 1 mm in diameter exposed to the liquid. The leakage current exceeds 100 nA already at low back-gate voltage. As seen later, the conductance through the wire is typically around $0.1 \,\mu$ S during sensitivity measurements, which corresponds to 100 nA for 100 mV V_{SD}. Thus, the leakage current ratio is too high without a protection layer. Covering the wafer with $\approx 13 \,\text{nm} \,\text{Al}_2\text{O}_3$ by ALD reduces the leakage current below picoamperes for a adequate back-gate voltage range. A series of samples with different protection layer thicknesses is shown in fig. 4.1b. The device with 100 ALD cycles ($\approx 11 \,\text{nm} \,\text{Al}_2\text{O}_3$) is already well protected from leakage current. Increasing the ALD layer thickness does not further reduce the leakage. Nevertheless, manufacturing errors gave rise to leakage in some cases. Whether it was due to bad epoxy and liquid channel sealing or due to pinholes in the ALD layer was not clear.

Comparing leakage current for different solutions showed that $|_{leak}$ is not depending on the concentration of protons, as long as the solution was an electrolyte, meaning it contained free ions. Reference measurements with ethanol showed nearly no leakage, due to missing ions (see fig. 4.2).



Figure 4.1.: Leakage current versus applied voltage in pH8 buffer solution. Voltage was applied in the liquid with a platinum electrode. The current was measured through the back-gate for (a) and through the wire for (b). Measurement setup is shown in fig. 2.6. a) Clean wafer with no structure on it. The reduction in leakage current after Al_2O_3 ALD is significant. b)Leakage current for different samples of batch A. 100 ALD cycles seem to be enough to reduce the leakage current below 1 nA which is sufficient for pH sensing where the signal current is \leq 100 nA in this back-gate range. No significant improvement can be observed if the number of ALD cycles is increased. a4 (\blacksquare) and a7 (\blacksquare) show only a little leakage current reduction, which is probably due to a manufacturing error during the liquid channel or the epoxy sealing process.



Figure 4.2.: Leakage current measured in different solutions. Voltage was applied at the liquid gate, current was measured at the back gate. Comparing pH4 and pH8 solutions, I_{leak} remained constant, meaning the numbers of protons has no large influence on leakage. The reference measurement with ethanol (EtOH) showed virtually no leakage current, due to missing ions (protons) in the solution.

4.2. Ion response

Increasing the ion concentration in an electrolyte changes the screening length and the double layer capacity at the SiNWFET-liquid interface according to eq. 1.14 and 1.15. To analyze the interaction of ions with the sensor surface, measurements in different salt concentrations were taken. Thereby the shifts in threshold voltage were compared.

Due to the lack of samples with good characteristics in the accumulation regime, most of the measurements were taken in the inversion regime. Series of potassium chloride (KCl) solutions over a large range of different concentrations were measured. Fig. 4.3b shows the sensitivity of sample a6w4 to KCl and sodium chloride (NaCl) in the n-regime. Comparing pure H_2O with KCl solutions showed that the ions shifted the SiNWFET threshold voltage. Higher ion concentrations seem to act as an additional negative gating and therefore increased the inversion threshold. We assumed that the shift was an effect of the selective absorption of anions (Cl⁻) at the surface. pH induced shifts were unlikely, since the pH values of the different electrolytes varied only in a small range (pH 6-7). The data was also plotted in log scale, because we assumed a similar behavior as for the pH measurements in the next section, where the threshold voltage shifts linearly with the log of the H⁺ concentration. The resulting sensitivity in mV gate shift per decade in ion concentration was up to the range of 90, which is quite high compared to further results. Fig. 4.3d shows that the sensitivity at fixed back-gate depends on the read-out area and varies from 11-97 mV/dec. This effect was only seen in inversion measurements and made the results less reliable. The difference in sensitivity for fixed liquid-gate (here varying from 67-97 mV/dec) is seen in all measurements. This is a characteristic of our device design and is explained in chapter 6.

Fig. 4.4 shows similar measurements with a sample of a previous produced batch. Here a smaller range of KCl concentrations from 0.1 mM up to 100 mM was used. This sample shows less sensitivity (From 54 mV/dec at fixed liquid gate and up to 85 mV/dec at fixed back-gate), but the results are in agreement with the results in fig. 4.3.

Fig. 4.5 shows the ion response of sample a5w4 measured in the accumulation regime. The trend for increasing ion concentration is less obvious. Whether this was an effect of poor sample quality was not sure. Fig. 4.5a indicates, that the liquid gate had a very small influence on the FET conductance and was hardly able to deplete the nanowire. The jump in threshold voltage from 10 mM to 100 mM could be due to the pH change of the electrolyte. The measured pH values decreased from \approx pH7 for H₂O to \leq pH6 for 1M ion concentration. At low concentration the pH was not well defined. For concentrations above 100 mM where the pH was nearly constant, the threshold voltage even slightly decreases. This trend stands in contrast to the other measurements.

In [14] a model of selective cation (K⁺ and Na⁺) adsorption is described. They assume that a SiO₂ surface, which has its point of zero charge in the range of pH 1-4, would be negative at pH \approx 7 and therefore attract cations selectively.

$$\equiv Si - O^{-} + Na^{+} \rightleftharpoons \equiv Si - O - Na$$
$$\equiv Si - O^{-} + K^{+} \rightleftharpoons \equiv Si - O - K$$

This model was supported with XPS studies in [32] where an accumulation of Na^+ ions was found in the double layer. This caused a depletion of mobile charge carriers (holes) in the p-type silicon which increased the electrical resistance and lowered the threshold voltage respectively. In the inversion regime such a cation accumulation would act the other way round and accumulate minority charge carriers (electrons) which causes a conductance increase and threshold voltage



Figure 4.3.: a) Conductance color coded map of sample a6w4 n-regime, measured in 200 mM KCI. The red lines indicate the conductance trace from which the threshold voltages were calculated. The white lines highlight the slope and indicate the capacitance ratio between back-gate and liquid-gate. The second kink at high V_{BG} and high negative V_{LG} is only seen in the n-regime. b) Threshold values for different ion concentrations (\blacksquare KCI, \triangle NaCI) plotted versus Log of millimolar lon concentration. For both salts V_{th} increases with higher concentration, which is an indication for CI⁻ accumulation at the surface. c,d) Threshold values for different fixed back-gate. Plotted on log scale (d) the sensitivity changes depending on the back-gate. This back-gate dependence is an effect of the inversion measurement and is not seen in accumulation regime measurements. e,f) Threshold values for different liquid-gates plotted in linear and log scale. There is a clear trend in threshold shift vs. KCI concentration. It is assumed that CI⁻ ions accumulate at the nanowire surface and act as negative gate. All the error bars describe the fitting errors and have no statistical origin.



Figure 4.4.: a) Conductance color coded map of the previous produced sample b1, measured in the n-regime in 5 mM KCl. b,c) Threshold values for different fixed back-gates vs. KCl concentration. Plotted on linear (b) and log scale (c). The slopes change depending on the back-gate. d,e) Threshold value for fixed liquid-gates +0.5 V and +0.9 V plotted in linear and log scale. As in fig. 4.3, also at lower ion concentrations, a clear trend of higher V_{th} with increasing KCl concentrations can be observed.



Figure 4.5.: Ion sensitivity. a) Conductance color coded map of sample a5w4 measured in 200 mM KCl. The liquid-gate showed a very weak influence on the conductance. b) Threshold voltages for different ion concentrations at fixed $V_{BG} = -3.1V$. c) V_{th} for fixed $V_{BG} = -3.1V$ versus the Log of the ion concentration in mM. d,e) Threshold voltages for fixed $V_{LG} = +1V$ plotted in linear and log scale. The ions shifted V_{th} , but no clear trend emerged. The error is quite large at fixed liquid-gate and very small at fixed back-gate, coming from the weak liquid-gate influence.

WFET surface was Al_2O_3 instead of SiO₂. The isoelectric point of an aluminum oxide surface is between pH 7 and pH 9 [33] which would leave the surface in a positive state at pH \leq 7. This would explain the results in fig. 4.3, 4.4 where a Cl⁻ accumulation in the double layer is assumed.

The ion response measurements were not absolutely reliable due to n-regime measurements on the one hand (back-gate dependent sensitivity) and weak liquid-gate influence on sample a5w4 on the other hand. Nevertheless, high sensitivities from 60 - 90 mV per decade in ion concentration were found. But further studies are needed to understand and quantify the underlying effect which caused the threshold shift.

5. Transport measurements in pH buffer solutions

For a quantitative approach the SiNWFETs were measured in different pH buffer solutions from pH4 to pH10. Thereby the sensitivity which is the threshold voltage shift in mV/pH could be determined.

5.1. pH sensitivity in the accumulation regime

For each pH a conductance plot as seen in fig. 5.1a was recorded. Threshold voltage values of cuts along a fixed V_{BG} or V_{ref} are taken as reference point to calculate the sensitivity in mV response per ΔpH . Hence, the slope of the linear fit through V_{th} versus pH was taken as sensitivity. Here the advantage of the dual gating comes into play, since the sensitivity depends on the read out section and direction. On the basis of such a conductance plot, the device-operating region can be tuned to an optimum.

Aluminum oxide is known to have a high surface buffer capacity [34, 35] which leads to a high interaction of the surface hydroxyl groups and the hydrogen ions in the solution. At low pH values, the Al_2O_3 hydroxyl groups are protonated. The additional charges on the surface shift the potential and act as a positive gate. At high pH values, the hydroxyl groups are deprotonated, which results in a negative surface potential and negative gating effect (fig. 1.1). With increasing pH values more surface hydroxyl groups are affected, thus the surface potential is changed to more negative values.

Sample a5w4 showed a weak influence of the liquid gate on conductance in the accumulation regime. This was seen in all the samples of batch A. Comparing fig. 5.1a and 5.2a it can be seen that sample a5w4 could not be depleted completely by the liquid gate, where s7w1 was already in depletion at low V_{ref} . The batch A samples also needed higher negative back-gate voltages (-3 - 7V) to get sufficient source-drain current (in the linear conductance regime) for accurate measurements. Regarding the pH induced surface potential shifts at fixed back-gate voltages (fig. 5.2b, red lines $\circ = 0V$, $\bullet = -3V$), the estimated sensitivities were in the same range and reached the Nernst limit ($\approx 60 \text{ mV/pH}$).

Considering the surface potential shifts at fixed liquid-gates (fig. 5.2b, blue lines V_{ref} : \blacksquare , $\blacksquare = -0.5 \text{ V}$, $\blacksquare = +0.5 \text{ V}$), the estimated sensitivities depended strongly on the readout area. In the high sensitive area ($V_{ref} = +0.5 \text{ V}$) the sensitivity exceeds 200 mV/pH, where at negative V_{ref} the pH dependent potential shifts are very diffuse and no actual sensitivity could be read out. (The red squared data was measured one day after the green data, but compensating this drift would not lead to a better sensitivity.) The high sensitivity could not only be explained by the surface potential shift on the surface, induced by the hydrogen ions. Also the gate coupling has to be taken into account, on which I will refer to in section 6.



Figure 5.1.: a) Conductance color coded map of sample a5w4 measured in pH7 buffer solution. The red lines indicate the conductance trace shown in (b) and (c). The white lines highlight the slope and indicate the capacitance ratio between back-gate and liquid-gate. Wire a5w4 shows a weak influence of the liquid gate. b) Conductance response for different pH values at fixed back-gate (V_{BG} = -3.2 V) while sweeping the liquid-gate. Conductance is plotted vs. the potential of the reference electrode. c) Conductance response for different pH values at fixed liquid-gate (V_{LG} = 0.81 V) while changing the back-gate stepwise. d) Threshold voltage values at accumulation for different pH values. The slope of the fits define the SiNWFET sensor sensitivity in mV/pH. The red lines indicate sensitivities for fixed back-gates (\blacksquare = -3.6 V, \bullet = -3.1 V) while sweeping the liquid-gate. The blue lines indicate sensitivities for fixed back-gates are very small and not visible at this scale.



Figure 5.2.: a) Conductance color coded map of sample s7w1 (120 ALD cycles) measured in pH7 buffer solution. The red lines indicate the conductance trace from which the threshold in (b) were calculated. The white lines highlight the slope and indicate the capacitance ratio between backgate and liquid-gate. b) Threshold values at accumulation for different pH values. The slope of the fits define the sensitivity of the SiNWFET sensor. The red lines indicate sensitivities for fixed back-gates (• = -3V, • = 0V) while sweeping liquid-gate. The blue lines indicate sensitivities for fixed liquid-gate ($\Box = 0.5V$, \blacksquare and $\blacksquare = -0.5V$ measured over two days. In this region the threshold voltage shifts are unconstant). The sensitivity depends on the read out section.

5.2. Measurements in the inversion regime

Batch A samples showed very weak response on the liquid gate in the accumulation regime. Hence, some measurements were performed in the inversion regime (positive V_{BG}). Here, the conductance map showed a contrary behavior. Fig. 5.3 shows that conductance is increased with increasing back- and liquid-gate, which is consistent with the image in fig. 1.1, since the conductance is dominated by minority charge carriers (electrons). The sensitivity seems to be comparable with the samples measured in accumulation. Sensitivities for fixed V_{BG} are constant around $\approx 50 \text{ mV/pH}$, whereas the sensitivities for fixed V_{LG} are strongly dependent on the read out section and direction, and vary from $\approx 24 - 128 \text{ mV/pH}$.

Nevertheless, measuring in inversion inclosed too many uncertainties to give reliable results. In fig. 5.3a a second kink in the conductance trace at positive V_{BG} and negative V_{LG} was visible. This kink was observable in most of the measurements performed in inversion. Is is thought to come from a high concentration of minority charge carriers close to the BOX layer. At a certain positive V_{BG} this concentration is too large to be depleted by the liquid gate. For several samples the sensitivities at fixed V_{BG} depended on the readout area (see fig. 4.3), which could not be observed in the accumulation regime. Additionally, the slopes' standard deviations were very large. Summing up, measurements in the inversion regime remained unreliable. Whether this were bad sample qualities or n-type conductance effects was not sure.

5.3. pH measurements with APTES coated surface

To sense specific molecules in further steps, the nanowire surface has to be functionalized. For example antigen and DNA detection needs immobilized antibodies and single-stranded DNA on the sensor surface. With such molecules the distance between charge and nanowire is larger and the charge density is most likely much smaller. Additionally screening of surrounding counter



Figure 5.3.: a) Conductance color coded map of sample a9w2 inversion (n-regime) measured in pH7 buffer solution. The white lines highlight the slope and indicate the capacitance ratio between backgate and liquid-gate. Sample a9w2 showed hardly any influence of the liquid gate on the conductance in the p-regime, but normal behavior in the n-regime. b) Threshold values at inversion for different pH values. The slope of the fits define the sensitivity of the SiNWFET sensor. The red lines indicate sensitivities for fixed back-gates (• = +2.2 V, • = +2.5 V) while sweeping the liquid-gate. The blue lines indicate sensitivities for fixed liquid-gate ($\Box = 0.4 V$, $\blacksquare = -0.4 V$).

ions damp the signal.

The first step of functionalization was to cover the sample with 3-aminopropyltriethoxysilane (APTES). APTES is also interesting for future experiments, since its amino residue is a good chemical linker group for surface functionalization. In this silanization process, the ethoxy groups bind covalently to the oxidized surface (the protocol is given in A.2). Modification of oxidized surfaces by covalent binding of silanes with surface silanol groups has been studied by several groups [36–39]. With APTES it resulted in a self assembled monolayer with freestanding amine groups. Now, the amine groups were protonated $(-NH_3^+)$ and deprotonated $(-NH^-)$ in addition to the hydroxy groups of the wire surface. Due to the reduction of interacting sites (one APTES binds ideally three hydroxy groups) and larger distance between the charge and the wire, a decrease in sensitivity was expected.

Fig. 5.4 shows that the conductance properties in air were changed. The threshold voltage was shifted by $\approx +3$ V. Large hysteresis arose with APTES coming from the changed nanowire surface. The organic layer is thought to trap charges and therefore increases hysteresis.

The pK_a value is the logarithm of the acid dissociation constant ($K_a = \frac{[NH^-][H^+]}{[NH_2]}$) and describes the dissociation equilibrium. After the Henderson-Hasselbalch equation

$$pH = pK_a + \log\frac{[NH^-]}{[NH_3]} \tag{5.1}$$

the concentration of NH₃ is equal to the concentration of NH⁻ when the pH is equal to the pK_a. Around the pK_a value the highest proton exchange at the amine group is expected. In literature pK_a values around 10 were found for APTES on silicon [40]. We have expected the pK_a for APTES on aluminum oxide to be in the same range. The pK_b value (NH₂ \rightarrow NH₃⁺) of APTES in solution is 3.63 [41].

pH measurements showed that the overall sensitivity of sample s7w1 was slightly decreased when the sample was covered with APTES (compare to fig. 5.2). But the sensitivity between pH 3-5 seems to be a little higher. This could be the pK_b range of APTES. Nevertheless, the

high total sensitivity and the smeared out pK signal indicated a strong background sensitivity from uncovered surface hydroxyl groups coming from APTES polymerization.

To prove the silanization process, surface tension tests on ALD coated test wafers were done. The untreated wafer showed a high hydrophobicity, resulting in a large contact angle. This was due to natural accumulation of organic residues when keeping the sample in air. The UVO treated wafer was silanized with different APTES-toluene concentrations (1:10, 1:100). Fig. 5.4b shows that silanization increased the contact angle of a waterdrop on the wafer surface. The reverse effect was seen after UVO treatment. 5 min UVO seemed to be enough to remove the silanes and leave the surface in a hydrophilic state.

The measurement showed, that it was possible to cover the Al_2O_3 in a silanization process and that a relative high pH sensitivity (up to $\approx 190 \text{ mV/pH}$) remained. It was not clear how dense the APTES monolayer was. It is expected that many uncovered aluminum hydroxyl groups participated in pH sensing. Further studies need to be done, (for example with silanes of different length and end groups) to investigate the dependence on the distance between the charge and the wire. Different silanization protocols or passivation of the remaining hydroxyl groups with alkanes could help to investigate the monolayer density. Measurements with quartz balance, ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) could be done to analyze the silanization.



Figure 5.4.: Sample s7w1 covered with 3-aminopropyltriethoxysilane (APTES). a) APTES monolayer shifts the conductance characteristics in air. The hysteresis is enhanced with APTES as the nanowire surface is changed. b) Contact angle measurements on a ALD test sample. The surface hydrophobicity is changed with APTES. 5 min UV ozone treatment is enough to remove APTES. c) Conductance color plot at pH7 d) Sensitivity of sample s7w1 with APTES. The sensitivity is slightly decreased with APTES coating compared to 5.2. □: Data measured one day later and not included in the sensitivity fit. Between pH 3-5 a slightly higher sensitivity was observed. This can be interpreted as pK_b of the amine group.

6. Interpretation of high sensitivity beyond the Nernst limit

As seen in section 5.1 the sensitivity could exceed 200 mV/pH, which is far beyond the Nernst limit of 59.2 mV/pH at room temperature. To explain such high shifts, the dual gate measurement has to be considered. A derivation of the gate interplay taken from [30] is given in the following section.

The large differences in sensitivity for fixed liquid-gate can be explained by the different influence of the gates. The gate interplay V_{BG}/V_{LG} could be calculated using the capacitance ratio C_{BG}/C_{LG} . This simplified term could also be interpreted as the slopes, indicated by the white lines in fig. 5.1, 5.2. Two main areas of different slopes could be deduced from the conductance plots. At less negative V_{BG} and $V_{LG} < 0$ the slope were steep (> 1). In this region, the SiNWFET was driven into depletion. While the back-gate affected the whole device, meaning also the contacts, the liquid-gate had only an effect on the wire. Approaching the depletion region V_{LG} became less effective, because the silicon leads (influenced by V_{BG}) suppressed the current through the FET. The dominance of V_{BG} led to a large gate capacitance ratio C_{BG}/C_{LG} ($\approx 5 - 10$). For negative V_{BG} the whole device including the leads was driven in accumulation and V_{LG} had an increased influence on the wire. For good samples, feasible for liquid measurements, the liquid-gate was able to drive the nanowire into depletion. Sample s7 showed a coupling ratio of ≈ 0.2 in this region.

Most of the produced samples showed extremely weak influence of the liquid-gate in the accumulation region. The SiNWFETs could not be driven in depletion, even at high $V_{LG} \approx +1.2 \text{ V}$. Higher voltage was not applied in liquid, because electrochemistry would have occured which could have affected the measurements. Nevertheless, those sample showed a relatively large liquid-gate influence in the inversion regime (see fig. 5.3).





Fig. 6.1 shows the capacitance model of our dual-gated system. Changing the pH of the solution adds charges Q_0 to the oxide surface according to fig. 1.1. The charge Q in the nanowire is influenced by Q_0 , V_{BG} and V_{LG} .

$$\frac{\delta Q}{\delta V_{BG}} = C_{BG} \cdot \frac{C_{NW}}{C_{NW} + C_{d/,ox} + C_{bg}}$$
(6.1)

$$\frac{\delta Q}{\delta V_{LG}} = C_{dl,ox} \cdot \frac{C_{NW}}{C_{NW} + C_{dl,ox} + C_{bg}}$$
(6.2)

where $C_{dl,ox}$ is the series connection of C_{dl} and C_{ox} . The dependence of Q on Q_0 can be written as follows:

$$\frac{\delta Q}{\delta Q_0} = \frac{C_{NW}C_{ox}}{C_{d/}(C_{NW} + C_{BG} + C_{ox}) + C_{ox}(C_{NW} + C_{BG})}$$
(6.3)

A change in bulk pH (pH_B) changes the surface pH (pH_S) which changes the surface charge density σ_0 and Q. Thereby, positive charge carriers δQ in the conduction channel are induced or removed. Hence the conductance G in the nanowire and therefore its threshold voltage is changed. Assuming V_{th} is back compensated by changing the gate simultaneously:

$$\partial p H_S \left(\frac{\partial Q_0}{\partial p H_S} \right) \left(\frac{\partial Q}{\partial Q_0} \right) + \delta V_{gate} \left(\frac{\partial Q}{\partial V_{gate}} \right) = 0 \tag{6.4}$$

From the α -factor in the Nernst equation 1.20 it can be written

$$\frac{\partial \sigma_0}{\partial \rho H_S} = -q\beta \text{ and } C_S := \frac{q^2\beta}{2.3kT}$$
(6.5)

where C_S is a defined surface capacitance with q as charge and β as buffer capacity. Combining equation 6.4 and 6.5 the potential shift at the gate can be calulated.

$$\delta V_{gate-shift} = \delta p H_S \left(\frac{2.3kT}{q}\right) \underbrace{\mathcal{C}_S \left(\frac{\partial Q}{\partial Q_0}\right) \left(\frac{\partial V_{gate}}{\partial Q}\right)}_{(6.6)}$$

R is a combination of C_S , eq.6.1 and eq.6.3. For the individual gates it can be written as

$$R_{LG} = \frac{C_S}{C_{dl}} \tag{6.7}$$

$$R_{BG} = \frac{C_{ox}C_{dl}}{(C_{dl} + C_{ox})C_{BG}} \left(\frac{C_S}{C_{dl}}\right) \text{ the ratio is then: } \frac{R_{BG}}{R_{LG}} = \frac{C_{dl,ox}}{C_{BG}}$$
(6.8)

Coming back to the Nernst equation which can be written depending on the gate

$$\delta V_{LG-shift} = \delta p H_B \left(\frac{2.3kT}{q}\right)^2 \alpha \tag{6.9}$$

$$\delta V_{BG-shift} = \delta V_{LG-shift} \left(\frac{C_{dl,ox}}{C_{BG}} \right)$$
(6.10)

With the dimensionless sensitivity parameter α . Taking all the capacitances into account and not only the double-layer capacitance as in eq.1.20, α can be written as follows:

$$\alpha = \frac{1}{\frac{C_{dl}}{C_{S}} + \frac{C_{dl}}{C_{dl} + \frac{C_{ox}(C_{NW} + C_{BG})}{C_{MW} + C_{BG} + C_{ox}}}}$$
(6.11)

In [13] $C_{dl} >> C_{ox}$, C_{NW} , C_{BG} so $\alpha^{-1} = 1 + C_{dl}/C_S$, and therefore $\alpha < 1$. But if β is extremely large, $C_S \rightarrow \infty$

$$\alpha \approx 1 + \frac{C_{ox}C_{NW}}{C_{dl}(C_{ox} + C_{NW})} , \text{ which can be larger than 1!}$$
(6.12)

Together with eq.6.9 this could explain the high sensitivities we found at fixed back-gate which were close to 60 mV/pH. β seems to be very large for the Al₂O₃ ALD top oxide. With eq.6.10 the high sensitivities of more than 200 mV/pH at fixed liquid-gate can be

With eq.6.10 the high sensitivities of more than 200 mV/pH at fixed liquid-gate can be explained. A shift at the liquid-gate is multiplied with the capacitance ratio $(C_{dl,ox}/C_{BG})$ and seen amplified at the back-gate. The amplification is given only by the capacitance ratio.

In a rough approximation this could be seen in the color coded conductance plots. The white lines indicate the gate coupling ratio V_{BG}/V_{LG} . Multiplying the sensitivity values for fixed liquid-gate with the coupling ratio gave a rough approximation of the sensitivities for fixed back-gate, as seen in fig. 6.3.

In the amplificated region pH induced shifts of V_{th} could be read-out more accurate due to higher electrical response. The sensitivity is increased while the read-out error stays in the same range. Since the capacitance ratio ($C_{dl,ox}/C_{BG}$) is proportional to the ratio of back-gate oxide and liquid-gate oxide layer (BOX/TOX) thickness, the apparent sensitivity could be tuned by varying these layer thicknesses. The maximum would be obtained with no top oxide layer, which on the other hand would enforce the leakage current problem. Increasing the BOX layer thickness changes the FET response on the back-gate. But higher back-gate voltages would be needed to reach accumulation. Tuning the buried oxide thickness ratio is not easy, since the BOX layer thickness is given by the wafer and can not be changed during the sample fabrication. The easiest way to tune the TOX layer thickness is changing the number of ALD cycles. Comparing samples a5 and s7 with 300 and 220 ALD cycles (\approx 33 and 24 nm Al₂O₃) the estimated coupling ratio (white lines in fig. 5.1, 5.2) is larger for thicker ALD layers. Sample s7 with less ALD cycles shows a higher sensitivity. However, the sensitivities can not be compared directly, since the sample characteristics in liquid were not the same.

Fig. 6.2 compares s7w1 with previous fabricated samples of different TOX layer thicknesses. The white lines and numbers indicate the ratio between the two gates. This ratio drops from 0.43 (for 80 nm silicon top oxide/13 nm Al_2O_3) to 0.29 (for 40 nm SiTOX/40 nm Al_2O_3) and down to 0.20 (for 40 nm SiTOX/24 nm Al_2O_3). We assumed that during the fabrication the SiO₂ top oxide is etched by 20 – 30 nm. The slope seems to correspond to the TOX/BOX thickness ratio, which supports our capacitance ratio model.

In a next step, the top oxide which was used as etching mask could be removed in order that the silicon area is enlarged and the sensitivity is further increased.

33



Figure 6.2.: Conductance maps in pH 7 buffer solution. a) Sample with 80 nm silicon top oxide and 13 nm Al_2O_3 ALD. This sample showed a maximum sensitivity of 96 mV/pH at fixed liquid-gate. b) Sample with 40 nm SiTOX and 40 nm Al_2O_3 ALD. This sample showed a maximum sensitivity of 130 mV/pH at fixed liquid-gate. c) Sample s7w1 with 40 nm SiTOX and 24 nm Al_2O_3 ALD. S7w1 showed a maximum sensitivity of 215 mV/pH. The white lines and numbers indicate the gate ratio.





7. Summary and conclusion

In this master thesis the properties of dual gated silicon nanowire field effect transistors (SiNWFET) were studied for future biosensing applications. Fabrication of SiNWFET sensor devices with reproducible properties were fabricated. Measurements in solutions of different pH gave information about sensitivity, leakage and gate influence. It was shown that Al_2O_3 atomic layer deposition shifted the conductance characteristics related to the gate voltage, reduced the leakage current through the system and increased the sensitivity of the devices, due to the higher buffer capacity of aluminum oxide. A sample series of different ALD layer thicknesses was fabricated to study the influence of Al_2O_3 thickness on the device properties. Due to production problems during the UV, bonding and epoxy processes, the yield of useful wires was very low (< 10%) and therefore no systematic ALD dependence on pH sensitivity could be estimated. Nevertheless, a trend to an increased threshold shift, as well as a change in transconductance with increasing ALD cycles could be observed while measuring in air. It was also found that 100 ALD cycles ($\approx 11 \text{ nm } Al_2O_3$) were sufficient to reduce the leakage current to picoampere for an adequate back-gate voltage range. Further it is expected that less ALD increases the sensitivity due to a larger gate capacitance ratio, as seen in fig. 6.2.

pH measurements showed the expected shift in threshold voltage (according to fig. 1.1) by varying the pH value of the solution. The dual gate approach had the advantage that all potentials in the systems were known and the interplay of the gate capacitances could be investigated. The gate space conductance plots allowed to read out sensitivities at different working points and the most sensitive area could be determined. Fixing the back-gate resulted in sensitivities close to the Nernst-limit ($\approx 60 \text{ mV/pH}$). But fixing the liquid-gate resulted in very diverse sensitivity values from $\approx 0 \text{ mV/pH}$ up to more than 200 mV/pH, depending on the read-out area. The sensitivities were far beyond the Nernst-limit. Taking the capacitances and the gate coupling into account, these high values can be normalized by the gate capacitance ratio. The achieved results show great promise for the detection of small surface changes in future work.

Due to insufficient useful samples, some wires were measured in the inversion regime, since the liquid-gate dependence at positive back-gate voltage was much higher. The results showed similar sensitivities, but some unclarities in the conductance plot characteristics (at large positive back-gate voltage) remained, which made the results less reliable. The weak liquid-gate influence in the p-regime of the batch A samples was assumed to come from high contact resistances due to bad aligning during the UV-lithography. It could not be attributed to a too thick ALD layer, since good results on a different batch with even thicker ALD layer were achieved in previous work.

lon sensitivity tests showed varying results. It was seen that ions in the solution shifted the threshold voltage, but the results were not consistent and need to be completed with further measurements to understand the exact process at the nanowire surface. It can be assumed that the slightly charged aluminum oxide surface at neutral pH attracts ions selectively, which causes a change in conductance through the wire.

silanes performed Tests for surface functionalization with were usina 3aminopropyltriethoxysilane (APTES). The larger distance between the charges and the wire, as well as the different functional group (1 NH_2 instead of 3 OH) involved in the hydrolysis, led to the assumption that the sensitivity is decreased. But only a small sensitivity reduction was observed. Therefore, high background sensitivity of uncoated OH groups is assumed. Hydrophobicity measurements on ALD coated test wafers showed that our silanization process worked and that APTES is removable in UV-ozone. In a next step, passivation with alkanes could show how much background sensitivity is contributed from free hydroxyl groups of the $A|_2O_3$ surface. Test with silanes of different chain length and functional groups will give a better understanding of the effects happening at the surface.

The results showed, that the dual-gate approach has many advantages. Sensitivity can go far beyond the Nernst limit and the optimal working point for sensing can be adjusted. Further, the potentials in the system are well controlled and leakage current can be measured directly. $Al_2O_3 ALD$ is a highly promising technique for SiNWFET. The leakage current could be reduced to a minimum while increasing the buffer capacity β , which contributes to the high sensitivity. The ALD process is well controlled and reliable.

Outlook Future work will enclose functionalized SiNWFET for sensing specific analytes, as well as differential measurements with passivated reference probes. The sensitivity could be further increased, by removing the silicon top oxide which was a leftover from the production process. Measurements with different types of ions could give information about the double layer capacitance.

The number of published papers relating to "nano biosensor", which is increasing rapidly, is a good indicator of research activity and interest. The possibility of cheap large scale production is a great motive force. The market which reaches from pharmaceutical and medical use to daily use products such as food deterioration detectors, contains huge financial potential. The idea of a "lab on a chip" where several medical tests could be performed simultaneously would be an important tool for early diagnosis.

Acknowledgments

I'd like to thank Prof. Christian Schönenberger who gave me the possibility to do my master thesis on this interesting project. A special thank goes to the "nanowire-team" Alexey Tarasov, Oren Knopfmacher and Wangyang Fu who introduced me into the topic and the techniques and methods in the lab. It was a pleasure working within this team. Further I'd like to thank Dr. Michel Calame for the interesting meetings and discussions which helped me to understand the background of the topic and aroused my interest. I also like to thank my office 0.23 and the whole Schönenberger-group for all their help, support and pleasant company.

l enjoyed my work and took much pleasure in scientific research.

Bibliography

- [1] Shuming Nie and Richard N. Zare. Optical detection of single molecules. *Annual Review of Biophysics and Biomolecular Structure*, 26(1):567–596, 1997.
- [2] Rachel McKendry, Jiayun Zhang, Youri Arntz, Torsten Strunz, Martin Hegner, Hans Peter Lang, Marko K. Baller, Ulrich Certa, Ernst Meyer, Hans-Joachim Güntherodt, and Christoph Gerber. Multiple label-free biodetection and quantitative DNA-binding assays on a nanomechanical cantilever array. *Proceedings of the National Academy of Sciences of the United States of America*, 99(15):9783–9788, 2002.
- [3] Scott E. Thompson and Srivatsan Parthasarathy. Moore's law: the future of si microelectronics. *Materials Today*, 9(6):20 – 25, 2006.
- [4] P. Bergveld. Development of an ion-sensitive solid-state device for neurophysiological measurements. *IEEE Transactions on Biomedical Engineering*, 17, 19070.
- [5] Simon Middelhoek. Celebration of the tenth transducers conference: The past, present and future of transducer research and development. Sensors and Actuators A: Physical, 82(1-3):2 – 23, 2000.
- [6] P. Bergveld. Thirty years of isfetology: What happened in the past 30 years and what may happen in the next 30 years. *Sensors and Actuators B: Chemical*, 88(1):1 20, 2003.
- [7] Sander J. Tans, Alwin R. M. Verschueren, and Cees Dekker. Room-temperature transistor based on a single carbon nanotube. *Nature*, 393(6680):49–52, May 1998.
- [8] Jing Kong, Nathan R. Franklin, Chongwu Zhou, Michael G. Chapline, Shu Peng, Kyeongjae Cho, and Hongjie Dai. Nanotube Molecular Wires as Chemical Sensors. *Science*, 287(5453):622–625, 2000.
- [9] Philip G. Collins, Keith Bradley, Masa Ishigami, and A. Zettl. Extreme Oxygen Sensitivity of Electronic Properties of Carbon Nanotubes. *Science*, 287(5459):1801–1804, 2000.
- [10] Xiangfeng Duan, Yu Huang, Yi Cui, Jianfang Wang, and Charles M. Lieber. Indium phosphide nanowires as building blocks for nanoscale electronic and optoelectronic devices. *Nature*, 409(6816):66–69, January 2001.
- [11] Yi Cui and Charles M. Lieber. Functional Nanoscale Electronic Devices Assembled Using Silicon Nanowire Building Blocks. *Science*, 291(5505):851–853, 2001.
- [12] Eric Stern, James F. Klemic, David A. Routenberg, Pauline N. Wyrembak, Daniel B. Turner-Evans, Andrew D. Hamilton, David A. LaVan, Tarek M. Fahmy, and Mark A. Reed. Label-free immunodetection with cmos-compatible semiconducting nanowires. *Nature*, 445(7127):519–522, February 2007.
- [13] P. Bergfeld. ; isfet, theory and practice. IEEE SENSOR CONFERENCE TORONTO, 2003.
- [14] Inkyu Park, Zhiyong Li, Albert P Pisano, and R Stanley Williams. Top-down fabricated silicon nanowire sensors for real-time chemical detection. *Nanotechnology*, 21(1):015501 (9pp), 2010.

- [15] Kangho Lee, Pradeep R. Nair, Adina Scott, Muhammad A. Alam, and David B. Janes. Device considerations for development of conductance-based biosensors. *Journal of Applied Physics*, 105(10):102046, 2009.
- [16] Oren Knopfmacher, Dino Keller, Michel Calame, and Christian Schönenberger. Dual gated silicon nanowire field effect transistors. *Proceedings of the Eurosensors XXIII conference Procedia Chemistry*, 1:678–681, 2009.
- [17] Dino Keller. Nano Field Effect Transistors as basic building blocks for sensing. PhD thesis, Universität Basel, 2007.
- [18] Oren Knopfmacher. Development of soi-wafer based nanowire field effect transistors for sensor applications. Master's thesis, Universität Basel, 2007.
- [19] R. Kühnhold and H. Ryssel. Modeling the ph response of silicon nitride isfet devices. *Sensors and Actuators B: Chemical*, 68(1-3):307–312, August 2000.
- [20] S Middelhoek, A A Bellekom, U Dauderstadt, P J French, S R in 't Hout, W Kindt, F Riedijk, and M J Vellekoop. Silicon sensors. *Measurement Science and Technology*, (12):1641, 1995.
- [21] Martin Hedegård Sørensen. Nanowire biosensor. Master's thesis, DTU Nanotech, 2009.
- [22] Kwok K. Ng Simon M. Sze. Physics of Semiconductor Devices, 3rd Edition. Wiley, 2007.
- [23] Bharath R. Takulapalli. Molecular sensing using monolayer floating gate, fully depleted soi mosfet acting as an exponential transducer. ACS Nano, pages –, January 2010.
- [24] John O. Bockris, Amulya K. N. Reddy, and Maria Gamboa-Aldeco. Modern Electrochemistry 1: Ionics, 2nd Edition. Plenum Press, 1998.
- [25] Xuan Thang Vu, Jan Felix Eschermann, Regina Stockmann, Ranjita GhoshMoulick, Andreas Offenhäusser, and Sven Ingebrandt. Top-down processed silicon nanowire transistor arrays for biosensing. *physica status solidi (a)*, 206(3):426–434, 2009.
- [26] Yu Chen, Xihua Wang, Mi Hong, Shyamsunder Erramilli, and Pritiraj Mohanty. Surfacemodified silicon nano-channel for urea sensing. Sensors and Actuators B: Chemical, 133(2):593 – 598, 2008.
- [27] Szu-Chieh Wang, Chao-Sung Lai, Cheng-En Lue, and Chia-Ming Yang. Single si₃n₄ layer on dual substrate for ph sensing micro sensor. In *Sensors Applications Symposium*, 2009. SAS 2009. IEEE, pages 61–64, 2009.
- [28] Cambridge NanoTech Inc. Savannah 100 & 200 Atomic Layer Deposition System User Manual. - Cambridge NanoTech Inc., 2007.
- [29] Mikko Ritala and Markku Leskelä. Atomic Layer Deposition Handbook of thin film materials. Academic Press, 2002.
- [30] Oren Knopfmacher, Alexey Tarasov, Wangyang Fu, Mathias Wipf, Björn Niesen, Michel Calame, and Christian Schönenberger. The nernst limit in dual-gated si-nanowire fet sensors. *Submitted to Nanoletters*, Submitted, 2010.
- [31] G. D. Watkins. Epr of a trapped vacancy in boron-doped silicon. Phys. Rev. B, 13(6):2511– 2518, Mar 1976.

- [32] Andrey Shchukarev. Electrical double layer at the mineral-aqueous solution interface as probed by xps with fast-frozen samples. *Journal of Electron Spectroscopy and Related Phenomena*, 176(1-3):13 – 17, 2010. Charging Issues in Electron Spectroscopies.
- [33] E. McCafferty and J. P. Wightman. Determination of the surface isoelectric point of oxide films on metals by contact angle titration. *Journal of Colloid and Interface Science*, 194(2):344 – 355, 1997.
- [34] Garrison Sposito. The Environmental Chemistry of Aluminum. Lewis Publishers, 1996.
- [35] RB Martin. The chemistry of aluminum as related to biology and medicine. *Clin Chem*, 32(10):1797–1806, 1986.
- [36] Maryanne Collinson, Edmond F. Bowden, and Michael J. Tarlov. Voltammetry of covalently immobilized cytochrome c on self-assembled monolayer electrodes. *Langmuir*, 8(5):1247– 1250, May 1992.
- [37] C. Schyberg, C. Plossu, D. Barbier, N. Jaffrezic-Renault, C. Martelet, H. Maupas, E. Souteyrand, M. H. Charles, T. Delair, and B. Mandrand. Impedance analysis of si/sio2 structures grafted with biomolecules for the elaboration of an immunosensor. *Sensors and Actuators B: Chemical*, 27(1-3):457 460, 1995. Eurosensors VIII.
- [38] Agnès Perrin, Véronique Lanet, and Alain Theretz. Quantification of specific immunological reactions by atomic force microscopy. *Langmuir*, 13(9):2557–2563, April 1997.
- [39] Anne E. E. Norström, Pasi J. Mikkola, Janis G. Matisons, and Jarl B. Rosenholm. Adsorption of an isocyanurate silane on e-glass fibers from ethanol and toluene. *Journal of Colloid* and Interface Science, 232(1):149 – 155, 2000.
- [40] Véronique Balladur, Alain Theretz, and Bernard Mandrand. Determination of the main forces driving dna oligonucleotide adsorption onto aminated silica wafers. *Journal of Colloid* and Interface Science, 194(2):408 – 418, 1997.
- [41] http://www.chemicalbook.com/ProductMSDSDetailCB8686147 EN.htm, March 2010.
- [42] Maxim V. Fedorov and Alexei A. Kornyshev. Ionic liquid near a charged wall: Structure and capacitance of electrical double layer. *The Journal of Physical Chemistry B*, 112(38):11868–11872, September 2008.
- [43] MicroChemicals. *Lithografie*. MicroChemicals, 2008.

A. Appendix

A.1. Fabrication

A.1.1. UV lithography

As adhesion layer for the photoresist, HDMS was used. The negative photoresist ma-N 415 from *Micro resist technology* (6:1 diluted in 70% Annisol and 30% 2-methoxy-1-methylmethylacetat) was spin-coated at 6000 RPM for 45s. Prebake at 95,1°C for 90 s The UV exposure was done with a *Süss Microtech MJB4* with a mercury lamp at a wavelength of 365λ for 10 s (6 s hard contact time)

The resist was developed in ma-D 332S for ca. 80 s

In a later step, the lithography for the contacts was done with undiluted ma-N 415, which was spin-coated at 4000 RPM for 40 s. The resist was then exposed to UV light for 13 s and developed up to 65 s.

During processing batch A, problems with the mask aligner occurred. The wires were not very well defined.

A.1.2. Metal evaporation

Chromium evaporation

The sample was mounted in the evaporator chamber (*PLS500-Labor System, Balzers Pfeiffe*). The sample was cooled with liquid nitrogen to a temperature below $0^{\circ}C$. Cr was evaporated until a 60 *nm* layer had grown on the sample.

Lift-off was done in $60^{\circ}C$ warm acetone. The lift-off didn't work well for batch A. Residues of chromium stuck between the structures and the pattern lines were not well defined, as seen in fig. A.1. This lead to suboptimal electrical and sensing properties.



Figure A.1.: Sample a6 from batch A. Problem with the mask aligner and the chomium lift-off process lead to residual metal flakes and rough structure borders.

Aluminum evaporation

The sample was mounted in the evaporator chamber. At low pressure($< 5 \cdot 10^{-6}$ mbar) an argon flow through the chamber was set. With an Ar-plasma sputter device, ions were accelerated for 70 s onto the sample to clean the silicon from native oxide. Afterwards, the sample was cooled with liquid nitrogen below 0°C. To lower the pressure in the evaporation chamber, titanium was evaporated while the sample was protected. At last, aluminum was evaporated at a rate of 5 Å/s until a layer of 100 nm Al accumulated on the sample.

Photoresist lift-off was done in $60^{\circ}C$ warm acetone.

A.1.3. Etching

Plasma etch

 SiO_2 was etched with CHF₃ plasma (100 W for 2:30 min). O₂ plasma was used to get rid of the residues which were formed during the SiO₂ etch.

Cr etch

As chromium etch solution, potassium permanganate (NaOH : $KnMnO_4$: H_2O - 3:2:12) was used. The sample was etched for 10 min while the solution was shaken.

SiO₂ etch in buffered HF

To remove the thin native oxide layer on the silicon surface, the sample was moisten in H_2O , dipped in buffered HF (1:20) for 10 s and then rinsed in water and IPA.

For etching the contact areas, meaning the 40 nm top oxide, the etching time was 3:30 min at an etching rate of \approx 40 nm/s.

SiO₂ etching usually changed the color from greenish to red. This was not observable for batch S and A when etching with HF, but could be seen clearly when etching with CHF₃ plasma. XPS measurements showed that the SiO₂ is completely removed either way, using HF or CHF₃ plasma, although the color is different. Etch rate tests on SiO₂ test wafers with gold reference structures on top showed an HF etch rate of \approx 40 nm/min. The height was measured with an alpha stepper.

Anisotropic Si etching

Tetramethylammonium hydroxide (TMAH) is used for Si etching. The samples were etched for 14 min in 25% TMAH in water, mixed with 10% IPA at 45°C under constant stirring. The anisotropic etching underetches the SiO₂ and exposes the <111> plane [43].

A.1.4. Atomic layer deposition

For the ALD process a Savannah 100 & 200 Atomic Layer Deposition System from Cambridge NanoTech Inc. was used. Before the ALD process, the sample was dipped in HF to remove the native silicon oxide. The sample was then built in the ALD chamber and heated up to 225°C at low pressure under a constant N₂ flow. In a first step, the precursor trimethylaluminum (TMA, $(CH_3)_3AI$) flows into the chamber and binds to hydroxy groups at the surface. The precursor is then pumped out. In a second step, pure H₂O flows into the chamber and exchanges the Al-C bonds with Al-O-Al bonds and Al-OH at the surface respectively. As side product CH₄ is formed

44



Figure A.2.: XPS alalyse of a reference SiO₂ wafer, an HF etched and a CHF₃ plasma etched wafer. It shows that buffered HF is very efficient in removing SiO₂. X-axis is energy scale, Y-axis is number of counts.

and pumped out. With such a cycle a very dense layer is grown all over the sample. The number of cycles determines exactly how thick the Al_2O_3 layer will be. Each cycle produces a maximum of 1.1 Å of Al_2O_3 depending on temperature. Thus, 100 cycles produce 11 nm of Al_2O_3 [28]. The thickness was changed from 50 cycles up to 400 cycles. Parameters:

Temperature	225° C	
N ₂ flow	20 sccm	
pulse	0	0.1s
wait		15s
pulse	2	0.04s
wait		12s
goto	0	#cycles

Table A.1.: ALD parameters. Number of cycles $\times 0.11 \approx \text{Al}_2\text{O}_3$ in nm.

A.1.5. Liquid channel

For the liquid channel, the negative photoresist AZ 826 MIF from AZ electronic materials was used. Spin-coated with 4000 RPM for 40 s and prebaked for 60 s at 110°C, the resist was exposed to UV for 5.5 s. After exposure, the sample was postbaked again for 60 s at 110°C. With AZ 826 MIF developer (DEAZ) which is a tetramethyl-ammoniumhydroxide solution, the photoresist was developed for 30 - 35 s. To harden the resist, it was again exposed to UV light for 30 s and heated to 190°C for 10 minutes.

The tetramethyl-ammoniumhydroxide (TMAH) developer contained the same base as it was used for Si etching. Etch tests showed that TMAH also affected the $A|_2O_3$ of the ALD layer. $A|_2O_3$ was etched with $\approx 5 \text{ nm/min}$ when dipped in DEAZ.

A.1.6. Bonding

For a good back-gate contact, the substrate layer was scratched from the top and bottom side. With conductive silver paste the sample was glued into a chip carrier. The contacts were bonded to the chip carrier pins with a K&S 4532A Digital wedge bonder.

Many samples got destroyed during bonding. The bonding breached the BOX layer and shortcircuited the back-gate, due to too large force. The following parameters worked well:

	Chip carrier	Sample contact							
Power	1.44	1.33							
Time	4	4.8							
Force	1.4	0.7							
Loop		1.7							
Tail		1.9							

Table A.2.: Bonding parameters for K&S 4532A Digital bonder

A.1.7. Epoxy sealing

EPO-TEK 302-3M 80Z, Polyscience AG was mixed A:B - 1 : 0.45. The mixture was outgased for 30 min and after one hour the chip carrier was slowly filled with epoxy. After 24h the epoxy was hardened and the sample was ready to use for liquid measurements.

A.2. Functionalization with APTES

The sample was given in an exsiccator with a 3-aminopropyltriethoxysilane solution (10 vol% APTES) in toluene). The exsiccator was then evaporated for 10 min and kept closed for another 10 min. To anneal the coating, the sample was heated in an oven for 30 min at 80°C To remove the APTES, the sample was treated with UV-ozone. Surface tension measurements showed that 5 min UVO were enough to remove the silane monolayer.

A.3. Produced samples

46

		1	1	1	1	1		1	1		1	1	r –		1	- 1	-	- 1	-	-		-	1	
	Remarks		no wire after bonding	covered with epoxy	weak wire (higher leakage current)	too weak LG	influence, maybe		measured over 2	days	inverse shift		non linear threshold	increase	Alcane	functionalization	Alcane	functionalization			no wire after bonding		APTES	no wire after bonding
sensitivity n-	site (fixed	Hd//hm								no trend		9-		128										
sensitivitv	n-site (fixed BG)	mV/pH								50		65		50										
sensitivity p-	site (fixed	hd//n						37	5		-17												200	
sensitivity n-	site (fixed	Hd/Nu						56			-74												55	
liauid	measurement n-						ç			yes	no sens. Meas	yes		yes								e current	olus 7days	
liauid	measurement p-						and I G influence	weak LG influence		no LG influence	yes	threshold crossed		weak LG influence								no, too much leakage	no APTES, APTES, p	
max	leakage	[A]			2.20E-11			2.00E-10			5.00E-09	6.00E-11		2.60E-11									6.00E-08	
Treshold shift	(accumulation) with AI D in air	Σ					1 05	1.73		-0.3	0.27	+		0.44							2.2	0.8	2.2/3.4	
total no.	Working wires (in air)	(0	0	0		~			4	-	4		4		3		4	3	4	4	1	4	2
-	ALD (cvcles)	(()	50	100	150			300		100	150	200		100		no		no	no	no	120	120	120+100	120
	Wire			1			~	4		2	~	4		2									-	
	Sample		-	2	ę		~	1.0	,	9	7	8		6		1		2	3	4	5	9	7	8
	Batch		Ø	a	ŋ		c	5 00	1	Ø	a	a		ŋ		s		s	s	S	s	s	s	s

Figure A.3.: Overview of the produced samples. Batch A was coated with different ALD layer thicknesses. It showed weak sensing properties in the accumulation regime throughout the whole batch, due to weak liquid gate influence. Batch S showed good properties, but only a few samples were processed to the end. Different tests, such as functionalization or problems during the process led to a high failure rate. Most of the wires did not survive the bonding and the epoxy sealing.