

POTASSIUM SENSING WITH MEMBRANE-COATED SILICON NANOWIRE FIELD-EFFECT TRANSISTORS

M. Wipf¹, R. L. Stoop¹, A. Tarasov¹, K. Bedner², W. Fu¹, M. Calame¹ and C. Schönenberger¹

¹Department of Physics, University of Basel, Basel, SWITZERLAND

²The Laboratory for Micro- and Nanotechnology, Paul Scherrer Institute, Villigen, SWITZERLAND

ABSTRACT

Ion sensitive field-effect transistors (ISFETs) based on silicon nanowires (Si NWs) with high-k gate oxide layers display surface hydroxyl groups which are known to be sensitive to variations in pH and electrolyte concentration. To specifically detect other species than protons, oxide surfaces need to be chemically modified. In this work, we use polyvinyl chloride (PVC) membranes with embedded ionophores to specifically detect potassium ions. We find a high response of -38mV/decade in KCl concentration. Control measurements with MgCl and pH demonstrate the selectivity of the ionophore.

KEYWORDS

ISFET, Silicon nanowire, chemical sensing, ionophores

INTRODUCTION

Since its first proposition by P. Bergveld et al. [1] in the 1970s, the concept of ion-sensitive field-effect transistors (ISFETs) has been demonstrated to be suitable for different sensing applications. Recent progress in micro- and nanofabrication has led to a true revival of the ISFET concept. ISFETs based on silicon nanowires are promising for applications in pH sensing [2, 3] as well as chemical and label-free biosensing [4, 5, 6]. The working principle is based on the gating effect induced by charged species at the sensor surface, which is changing the current within the channel of the transistor.

We investigate the sensing properties of ISFETs based on silicon nanowires with high quality oxide layers of Al_2O_3 . Oxide surfaces are well-known to be very sensitive to variations in pH due to their high density of hydroxyl-groups. This observation can be understood by the site-binding model, which predicts a maximum possible shift in surface potential due to a change in pH of 59.5mV/pH (Nernst limit) at room temperature [7]. For both oxide surfaces, we demonstrate a pH response at the Nernst limit using a dual-gate approach [2]. Besides protons, other ions present in the electrolyte may influence the sensor's signal. We investigated the influence of the ionic strength of the background ions on the sensor response at a fixed pH. Interestingly, we find a non-linear response indicating non-specific adsorption of anions of the electrolyte, which can be described by an extension of the site-binding model [8]. While expanding the sensing capabilities to other species than protons, it is crucial to account for such contributions from the background electrolyte.

In this work, we functionalize Si nanowire ISFETs with Valinomycin ionophores embedded in a polyvinyl chloride (PVC) membrane to achieve a specific potassium ion (K^+) sensing. We demonstrate a response of

$\approx -38\text{mV/decade}$ for increasing KCl concentration. Having both functionalized and uncovered NWs (control) on the same sample allows us to monitor the contribution of the background electrolyte. Thereby we can extract the signal caused by the targeted potassium ion.

DEVICE FABRICATION

The samples were fabricated following a top-down approach on p-doped silicon-on-insulator wafers (SOI, Soitec, France). The buried oxide layer (BOX) has a thickness of 145nm . The 85nm thick p-doped device Si layer has a resistivity of $8.5\text{-}11.5\Omega\text{cm}$. First, the Si device layer was thermally oxidized to achieve a SiO_2 layer with thickness of 15nm . The nanowire pattern was written in a negative resist by electron beam lithography and transferred to the SiO_2 layer by reactive ion etching. The structured SiO_2 layer functions as an etching mask for the wet chemical etching of the Si device layer performed in tetra-methyl ammonium hydroxide (TMAH) with $10\text{ vol}\%$ isopropanol (IPA) at 45°C . The resulting NWs with (111) side faces were $6\mu\text{m}$ in length, 85nm in height and of different width ranging from $100 - 1000\text{nm}$. Each sample consists of four arrays with 12 nanowires each sharing a common drain contact for a total of 48 nanowires (Figure 1). The source and drain contacts were implanted with BF_2^+ ions at a dopant dose of $2.3 \cdot 10^{15}\text{cm}^{-2}$ and energy of 33keV . Thermal annealing in forming gas (6min at 950°C) was performed to activate the dopants.

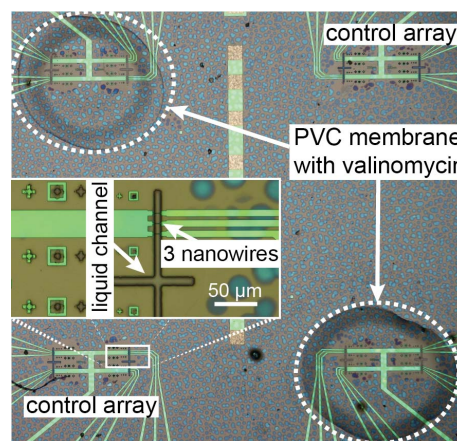


Figure 1: Optical image of a sample with four arrays consisting of 12 NWs after functionalization. Two arrays were covered by PVC membranes with Valinomycin. The two other uncovered arrays contain NWs with bare Al_2O_3 surface used for control measurements. Inset: Zoom of a control array revealing three NWs and the aligned liquid channel on top of the wires.

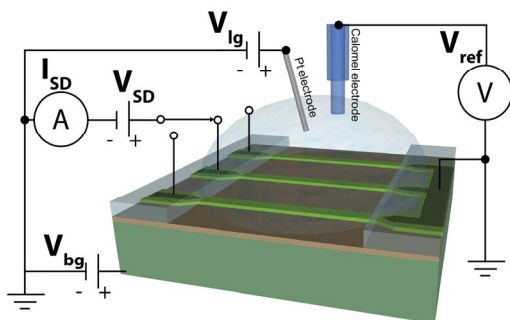


Figure 2: Measurement setup illustrated for three NWs. A source meter is used to apply a source-drain voltage and to measure the source-drain current. The device is gated by the back gate voltage (V_{bg}) applied to the Si handle wafer and by the liquid gate (V_{lg}) applied to a Pt wire immersed in the liquid. A Calomel reference electrode is used to precisely measure the electrical potential of the liquid (V_{ref}).

We use atomic layer deposition (ALD) to cover the sample by a thin layer (20nm) of Al_2O_3 at 225°C (Savannah S100, Cambridge NanoTeck). By optical lithography, the structure of the source and drain contacts were defined in the resist AZ nLOF 2000 to etch the ALD layer at the contacts in buffered hydrofluoric acid (BHF). The metallization of the source and drain contacts was done with Al-Si (1%). The formation of ohmic contacts was completed by a thermal annealing step at 450°. To ensure leakage free operation in liquid, a 2 μ m thick protection layer (SU-8 2002, MicroChem) with 6 μ m wide openings (liquid channels) was defined by optical lithography. Finally, the samples were wire bonded into a chip carrier and the bonds were sealed with epoxy (Epotek 353ND).

EXPERIMENTAL

Surface Functionalization

For the PVC membranes a mixture of Valinomycin (1.3%), polyvinyl chloride (PVC, 30.4%), Bis(1-butylpentyl) adipate (BBPA, 68.3%) was dissolved in cyclohexanone (50%) and tetrahydrofuran (THF, 50m%). All chemicals were purchased at Fluka. This mixture was deposited on individual NW arrays of UV/ozone treated samples (20min) by microdrop functionalization with a hamilton syringe (~0.2 μ l). The membranes were then cured for 24h at 50°C. As highlighted in Figure 1, only two of the four arrays of NWs were covered by the membrane. The two uncovered arrays were used as a control.

Electrical Measurements in Liquid

As depicted in Figure 2 a source-meter (Keithley 2636A) is used to apply a constant source-drain voltage $V_{sd}=100$ mV and to measure the source-drain current I_{sd} through the nanowire channel. Thanks to a switching-box (Keithley 3706) we are able to measure up to 48 NWs. To

set the operational point of the transistors accurately, we use a dual gate approach [2]. A back gate voltage V_{bg} is applied to the handle wafer. For all measurements, we set $V_{bg}=0$. Furthermore, a liquid gate V_{lg} is applied to a platinum wire immersed in the electrolyte. To monitor the electric potential of the liquid, we additionally use a calomel reference electrode V_{ref} (REF200, Radiometer analytical).

A peristaltic pump (MCP, Ismatec) and a valve selector system (CHEMINERT VICI, Valco Instruments Co. Inc.) were used to exchange solutions in the fluidic system. All devices are controlled by a personal computer which allows automated measurements using a custom-made LabView program.

For the different salt solutions we dissolve KCl (ACS 99.0 – 100.5%, Alfa Aesar) and $MgCl_2^+$ in deionized water (resistivity =17M Ω cm) resulting in a solution with ~pH 6.

RESULTS AND DISCUSSION

By micro-drop functionalization of single NW arrays with the ionophore embedded in the PVC membrane, the NWs become sensitive to potassium ions (K^+). Figure 3 shows the subthreshold conductance G of a Valinomycin-coated NW against the liquid potential V_{ref} in KCl electrolyte solutions with different concentrations.

The transfer curve shifts to the left with increasing KCl concentration. Since the NW ISFETs are p-doped and operated in accumulation, the shift of the transfer curve to the left indicates adsorption of positive charges at the surface.

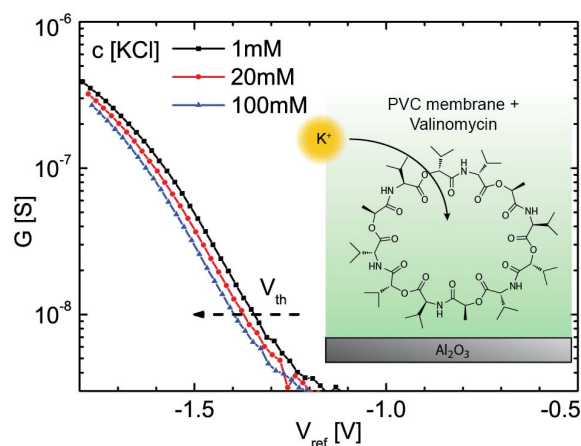


Figure 3: Conductance G vs. V_{ref} for a NW covered by the PVC with Valinomycin. The curves shift to the left for increasing salt concentration. Inset: Schematics of Valinomycin embedded in a PVC membrane on a NW.

To compare the functionalized NWs with the control NWs, we use the threshold voltage V_{th} as a figure of merit. The threshold voltage is defined at a constant value of $G = 10$ nS as indicated by the black arrow in Figure 3.

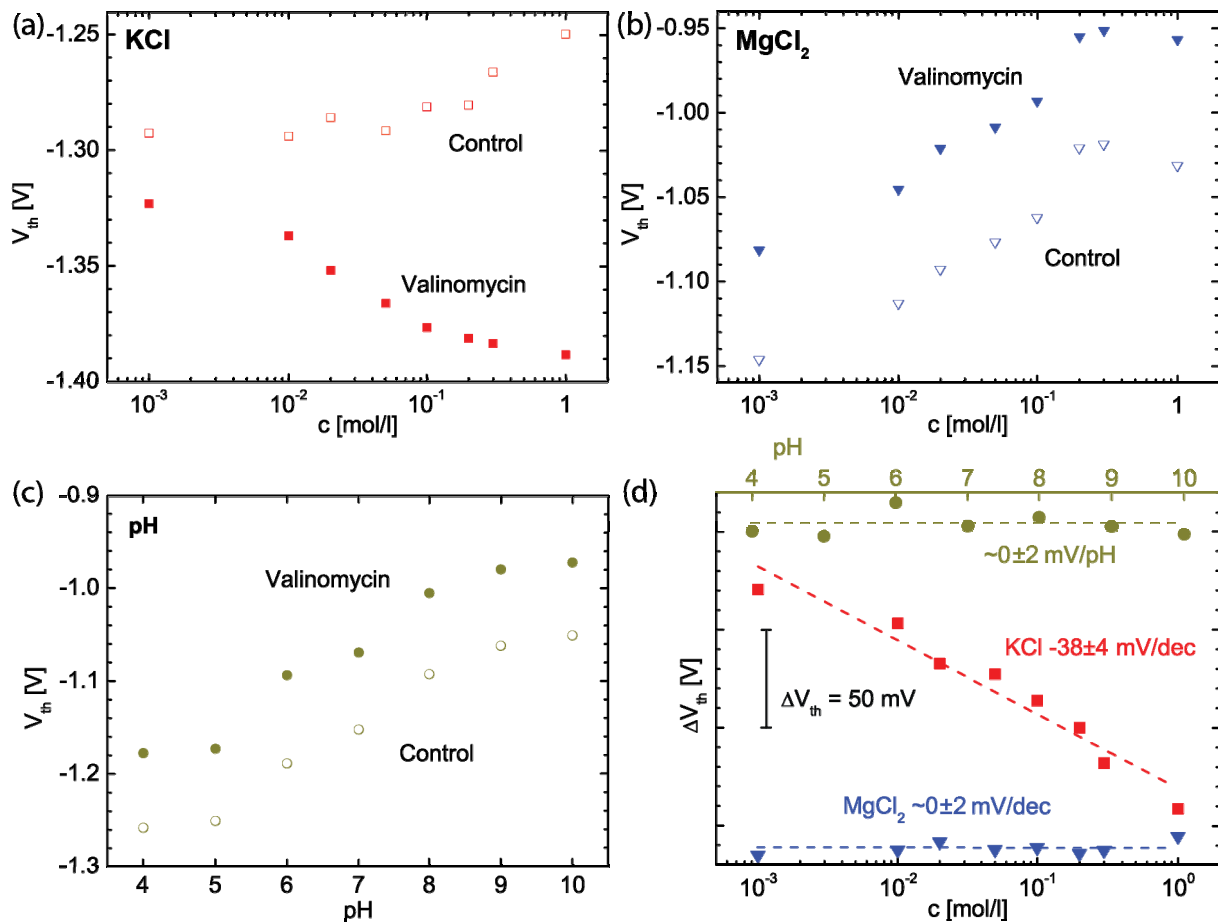


Figure 4: (a) V_{th} for a Valinomycin-functionalized NW and a control NW with bare oxide surface vs. increasing KCl concentration. While the control shows the characteristic shift towards positive V_{th} indicating anion adsorption, we observe an opposite behavior for the ionophore-covered NWs. (b,c) Control measurements for increasing $MgCl_2$ concentration and for solutions with increasing pH demonstrate the good selectivity of the ionophore towards K^+ ions. (d) Subtracting the signal of the control NW from the signal of the Valinomycin coated NW ($V_{th,Valinomycin} - V_{th,control}$) reveals the high response to KCl and no response to $MgCl_2$ and protons.

Figure 4a shows the shift in threshold voltage V_{th} with increasing KCl concentration for a Valinomycin-functionalized NW and a control NW. Solid squares correspond to Valinomycin coated NWs which show a negative shift with increasing KCl concentration due to K^+ adsorption. Empty squares show the response of a NW with bare Al_2O_3 surface of the control array. We attribute the positive shift at concentrations above 10mM to unspecific chloride adsorption at the oxide surface [8]. To investigate the specificity of the ion-binding membrane in more detail, a control measurement with $MgCl_2$ solutions was done, shown in Figure 4b. Both Valinomycin coated wires (filled triangles) and control wires (empty triangles) show a positive shift in V_{th} with increasing $MgCl_2$ concentration, indicating adsorption of Cl^- according to the model described in [8]. This shows that the PVC membrane is permeable to Cl^- ions. Hence the membrane does not passivate the oxide surface against the adsorption of chloride ions. A similar behavior is observed when repeating the measurement with different pH solutions (Figure 4c). Both surfaces respond in the same way, hence the ionophore PVC membrane is also permeable for protons. To obtain the response of the membrane we have to subtract the contribution of this two species from the

measured signal. As a new figure of merit we therefore introduce the differential shift in threshold voltage $\Delta V_{th} = V_{th,Valinomycin} - V_{th,control}$ as shown in Figure 4d. A response of -38mV/decade to a change in K^+ concentration is achieved. The differential threshold data for $MgCl_2$ in Figure 4d emphasizes the insensitivity of Valinomycin to Mg^{2+} . Also the second control measurement with varying pH confirms the high selectivity of the ionophore.

CONCLUSION

In conclusion, silicon nanowire field-effect transistors were modified for alkaline ions recognition. We show a selective potassium ion sensing with high response of -38mV/decade in the concentration range of 1mM up to 1M. The response for the target analyte is at least an order of magnitude larger than for the control species. We find that the PVC membrane is permeable for chloride ions and protons. This means that the hydroxyl groups of the oxide surface can still interact with H^+ and Cl^- when measuring in KCl solution and influence the response of the sensor. Thanks to control NWs, we are able to subtract

this background contribution to reveal the signal caused by the specific adsorption of potassium ions.

Our work shows the potential of nanostructured ISFETs covered with membranes for specific ion detection. Further we demonstrate the importance of differential characterization.

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CONTACT

*M. Wipf, tel: +41612673780;
mathias.wipf@unibas.ch