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Effect of microwave-assisted silanization on sensing properties of silicon nanoribbon FETs

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ABSTRACT

An important concern with using silicon nanoribbon field-effect transistors (SiNR FET) for ion-sensing is the pH-response of the gate oxide surface. Depending on the application of the FET sensor, this response has to be chemically manipulated. Thus in silicon oxide-gated pH-sensors with integrated sensor and reference FETS, a surface with high pH-sensitivity, compared to the bare gate oxide, is required in the sensor FETs (SEFET), whereas in the reference FETs (REFET) the surface has to be relatively pH-insensitive. In order to control the sensitivity and chemistry of the oxide surface of the nanoribbons, a silanization reagent with a functional group is often self-assembled on the SiNR surface. Choice of a silanization reaction that results in a self-assembled layer on a silicon oxide surface has been studied extensively over the past decades. However, the effect of various self-assembled layers such as monolayers or mixed layers on the electrical response of SiNR FETs in aqueous solution needs to be exploited further, especially for future integrated SEFET/REFET systems. In this work, we have performed a comprehensive study on 3-aminopropyltriethoxysilane (APTES) silanization of silicon oxide surfaces using microwave (MW) heating as a new biocompatible route to conventional methods. A set of complementary surface characterization techniques (ellipsometry, AFM and ATR-FTIR) was used to analyze the properties of the APTES layer deposited on the silicon surface. We have found that a uniform monolayer can be achieved within 10 min by heating the silanization solution to 75 °C using MW heating. Furthermore, electrical measurements suggest that little change in device performance is observed after exposure to MW irradiation. Real-time pH measurements indicate that a uniform APTES monolayer not only reduces the pH sensitivity of SiNR FET by passivating the surface silanol groups, but also makes the device less sensitive to cation concentration in the background electrolyte. Our silanization route proves promising for future chemical surface modification of on-chip REFETs.

1. Introduction

After the introduction of the ion-sensitive field-effect transistor (ISFET) biosensor by Bergveld [1], silicon nanoribbon (SiNR)-based ion sensing has gained considerable interest as an emerging field of biotechnology for ultrasensitive, label-free, electrical detection of biological and chemical species [2]. For example, a SiNR biosensor FET can be used in disease diagnosis after the surface of the nanoribbons has been modified with selective capture reagents (biomolecules), such as a DNA probe or an antibody [3]. For a recent review see Refs. [4–6].

The sensing mechanism underlying such detection can be understood in terms of changes in the surface charge density, which induces a change of the perpendicular electric field strength at the SiNR surface. The conductance of the SiNR changes due to depletion or accumulation of charge carriers along the nanoribbon channel caused by protonation/deprotonation of the surface active groups.

A SiNR ISFET with a silicon oxide gate is known to have a non-Nerstian and relatively low pH response [7]. However, the pH response of silicon oxide can be changed by self-assembly of a coupling agent on the surface [8]. The most commonly used organosilane agent is 3-aminopropyltriethoxysilane (APTES) [9]. The most widely used method of silanization is solution phase deposition through hydrolysis of the ethoxy groups of APTES in presence of water molecules adsorbed on the surface. The resulting APTES silanol groups condense and form Si—O—Si bonds with the surface silanol groups and form a film [10]. The density and

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orientation of the molecules within this film can significantly affect the pH response of the surface. In a perfectly ordered monolayer (0.7 nm thick), the APTES molecules are found with the amino groups oriented away from the oxide surface. These amino groups can be both available in free, unprotonated form, or can be protonated and form hydrogen bonds with silanol groups close to the surface [11].

Depending on the application of the silicon oxide-gated SiNR FET, various silanization routes can be utilized to change the sensitivity of the surface. For example, in an ion-sensitive FET (ISFET), a surface with a large pH response is required. Since silicon oxide has low pH-sensitivity, it is better to form a mixed film with two different active groups on the surface. In a reference FET (REFET) on the other hand, the surface silanol groups of the bare silicon oxide gate need to be passivated and by forming a uniform monolayer, the surface can be chemically modified to be pH-insensitive around the pH of point of zero charge.

The most effective method of silanization is a combined anhydrous deposition and in situ heating which not only promotes binding of APTES molecules but also increases the molecular density on the oxide surface of the nanoribbons. Heating of the solution upon sample immersion is achieved through conventional heating in an oil bath [12].

A critical factor in the conventional method is the heating rate, i.e. rapid heating is expected to improve the deposition of APTES during the silanization process. Thus, to take advantage of rapid heating, applying a heating method with an increased heating rate would be favorable.

It is known in organic chemistry that certain solutions can be heated up much faster using microwave (MW) irradiation [13]. In recent years the same MW based chemistry technique has been implemented into surface functionalization of substrates in solution [14]. In a comparative study on MW-assisted versus conventional heating, the grafting of alkyltrimethoxysilanes onto silica nanoparticles was investigated. An enhancement of the reaction rate as well as of the number of grafted molecules using MW irradiation was observed [15]. This enhancement was suggested to be a result of accelerated autocondensation of alkoxysilanes in presence of microwaves. Structural differences in the grafted layer assisted by MW heating compared to conventional heating were speculated but the wetting properties of the functionalized surface were not affected. No study on APTES silanization of SiNR surface using MW irradiation has been reported until now.

In this work, we present a new route toward silanization of SiNRs with APTES using MW irradiation as heating source. A set of complementary surface characterization techniques was used to analyze the APTES layer deposited on the silicon surface. The thickness of the APTES film was measured using ellipsometry. Atomic force microscopy (AFM) was used to study the film morphology and attenuated total reflection (ATR) mode of Fourier transform infrared (FTIR) spectroscopy was used to investigate the structure of the outermost layer of APTES. Furthermore, fluorescence images were taken from the as-deposited APTES layer attached with single-stranded DNA probes and hybridized with complementary DNA strands containing a fluorophore. Following surface characterization, SiNR-FETs were functionalized using the new MW-assisted route and the effect of the chemical modification of the silicon oxide surface using APTES on the pH sensitivity of the device in aqueous solution was investigated.

2. Experimental

2.1. Schottky barrier silicon nanoribbon FET fabrication

The SiNR FET devices were fabricated using SOI (silicon on insulator) wafers with a buried oxide thickness of 145 nm and a low boron doping level of 10^{15} cm^{-3}. The top-silicon layer was thinned down by dry thermal oxidation and HF etching to a final thickness of 30 nm. Nanoribbon structures were patterned on the device layer using lithography and subsequent dry etching. The nanoribbon length ranged from 1 to 100 μm while the width varied in the range of 1–10 μm (30 nanoribbons on each chip with some variations in nanoribbon geometry). The gate oxide was formed by dry thermal oxidation at 900 °C, leading to a final thickness of 8 nm. Contact pads were patterned by lithography using a double layer lift-off resist. The oxide on top of the silicon contacts was removed by wet chemical etching in hydrofluoric acid. Metallization was done using thin film vapor deposition of 20 nm of titanium as adhesion layer followed immediately by 200 nm of gold forming the Schottky contact on the silicon pads. Finally, a double layer of SU8 was patterned on the device using lithography. A thin 5 μm SU8 passivation layer with openings on each single nanoribbon limits the sensing only to the nanoribbon area and prevents leakage of current to the solution. A further thick 100 μm SU8 layer was also patterned. This layer contains microfluidic channels that run through all the wires. Both layers were hard-baked at 150 °C to ensure good adhesion between the two layers and also to the device. A separate polydimethylsiloxane (PDMS) layer was aligned on top of the nanoribbon chip forming a lid for the microfluidics which was punched with inlet and outlet holes for tubing of analytical solutions to the chip.

2.2. Sample preparation

Design limitations caused by the microfluidic layer and size of the nanoribbons make it impossible to perform surface characterization on the chips. Instead of the NRs we used control samples with the same surface properties. Control samples were prepared by dry oxidation of silicon wafers (polished (1 0 0), p-type, 1–10 Ωcm) at 900 °C for 15 min. The wafers were cut into 1 cm × 1 cm. The oxide thickness of 8 nm, measured by ellipsometry, was consistent with the silicon oxide thickness of the nanoribbons.

Control samples and silicon nanoribbon FETs were cleaned with acetone in a sonication bath for 10 min, rinsed with DI water and dried under nitrogen flow. Oxygen plasma cleaning was applied for 3 min (using a Plasma Cleaner from E.A. Fischione Instruments, Model 1020 where the flow rate is factory set) in order to remove organic contaminants and to activate the surface silanol groups prior to the silanization.

2.3. Microwave-assisted silanization

APTES silanization was performed under anhydrous conditions at high temperature using a Biotage Initiator^{TM} 2.5 single-mode microwave synthesizer. Following plasma etching, the cleaned and activated pieces were immediately placed in 10–20 ml microwave vials and a solution with a concentration of 1% (v/v) APTES in anhydrous toluene was added. Moisture was excluded through vacuuming and filling each sealed vial with dry nitrogen. Initiation of the silanization was carried out through rapid heating at a maximum power of 400 W until the set reaction temperature of 75 °C was reached after which the temperature was kept constant by modulating the MW power until the end of the silanization reaction. The surface temperature of the MW vial was measured using an infrared pyrometer. At the end of the set silanization time, the vials were cooled down by exposure to pressurized air.

To remove physisorbed APTES, post-silanization cleaning was carried out by sonicating the silanized samples two times for five minutes in anhydrous toluene followed by ethanol rinsing and drying under nitrogen flow. The silanized samples were incubated overnight in an oven at 110 °C under ambient atmosphere. Post-incubation is not only an important step in removal of residual