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Highly sensitive sensors for alkali metal ions based on complementary-metal-oxide-semiconductor-compatible silicon nanowires

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Highly sensitive sensors for alkali metal ions based on complementary-metal-oxide-semiconductor-compatible silicon nanowires (SiNWs) with crown ethers covalently immobilized on their surface are presented. A densely packed organic monolayer terminated with amine groups is introduced to the SiNW surface via hydrosilylation. Amine-modified crown ethers, acting as sensing elements, are then immobilized onto the SiNWs through a cross-linking reaction with the monolayer. The crown ether-functionalized SiNWs recognize Na^+ and K^+ according to their complexation ability to the crown ethers. The SiNW sensors are highly selective and capable of achieving an ultralow detection limit down to 50 nM, over three orders of magnitude lower than that of conventional crown ether-based ion-selective electrodes. © 2007 American Institute of Physics. [DOI: 10.1063/1.2746962]

Over the past years, ultrasensitive sensors based on nanoscale structures such as nanowires (NWs),¹ carbon nanotubes (NTs),² and nanoparticles³ have been widely investigated. These one-dimensional structures such as the NWs and NTs offer their potential for real-time and label-free sensing applications, and more attractively their suitability for large scale and high-density integration. Silicon nanowire (SiNW)-based sensors, in particular, have attracted much attention due to their capabilities of sensitive detection of biological and chemical species.^{4–6} Most of the studies involving “bottom up” fabrication techniques, however, suffer from certain limitations such as device-to-device uniformity, reflecting the variations in the device fabrication processes. Poor device uniformity, yield, and scalability hinder further development of these sensors into practical systems. Large scale fabrication of SiNW devices requires precise control at nanoscale where positioning, circuiting, and integrating individual nanodevices are some of the technical challenges. Developing a reliable and scalable fabrication technique for producing uniform and well-aligned SiNWs, integrating individual SiNW into functional devices with high yields, is one of the great challenges facing development of the next generation SiNW sensors.

Furthermore, one area that remains largely unexplored to date is the applicability of SiNW devices in clinical relevant metal ion sensing. Only calcium ion (Ca^{2+}) was studied using SiNW field effect transistors by immobilizing calmodulin as Ca^{2+} receptor onto the SiNW surface. The presence of 25 μM Ca^{2+} resulted in a merely 3% drop in conductance, precluding from further development.⁴ The ability to increase significantly the signal intensity is important for the realization of practical SiNW sensors.

Crown ethers are well-known ionophores for metal ion sensing.⁷ They have been widely studied in macrosystems since they feature inherent metal ion selectivity; a ring that is able to only complex metal ions with a very specific size. Many crown ethers have been synthesized and utilized in ion-selective electrodes (ISEs),⁸ crown ether dyes,⁹ and

crown ether-based ionophores for fluorescence sensing.¹⁰ It would be interesting to see how crown ethers behave in a nanodevice. For example, how crown ether-functionalized SiNWs respond to metal ions. Such chemical systems could, in principle, be used as clinical sensors, for *in situ* and in real-time detection of alkali metal ions of clinical relevance, such as Na^+ and K^+ as Na^+ and K^+ are widely used to monitor aberrant physiologies associated with diabetes, dehydration, diarrhea, and acute and chronic renal failure.¹¹

We have recently developed a complementary metal oxide semiconductor (CMOS)-compatible technology for forming arrays of SiNWs which are electrically addressable on an individual basis.¹² With the crown ethers (15-crown-5 and 18-crown-6) covalently immobilized on the SiNW surface, it is demonstrated in this work that the SiNWs function essentially as nanosensors for alkali metal ions (Na^+ and K^+) with much improved sensor performance. In addition, the SiNW sensors can readily be integrated in a portable system for specific and highly sensitive detection of alkali metal ions in a clinical setting.

The SiNWs (*n*-type) are fabricated by self-limiting oxidation process of silicon beams patterned using conventional deep ultraviolet photolithography.¹² An array of the CMOS-compatible SiNWs employed in this work for alkali metal ions sensing are shown in Fig. 1. Figure 1(a) represents a scanning electron microscopic (SEM) image of the array of SiNWs integrated with metal pads. As seen in Fig. 1(a), the fine lines on the right side correspond to the NWs, and the broad lines on the left side correspond to the metal pads for electrical contacts. Our fabrication process produced SiNWs with a 5–10 nm SiO_2 coating on their surface. The SiNW array was 200 μm in length with 2 μm of spacing in between. They were anchored on a silicon-on-insulator wafer perfectly and were regularly shaped with an almost identical diameter of 30 nm. As shown in Fig. 1(b), an atomic force microscopic (AFM) image further visualizes the individual nanowires and the nanowire array. To better demonstrate the high uniformity of the SiNWs, *z* axis in the AFM image was substantially stretched compared with *x* and *y* axes. Even at this abnormally amplified scale, only slight unevenness of the SiNWs was observed.

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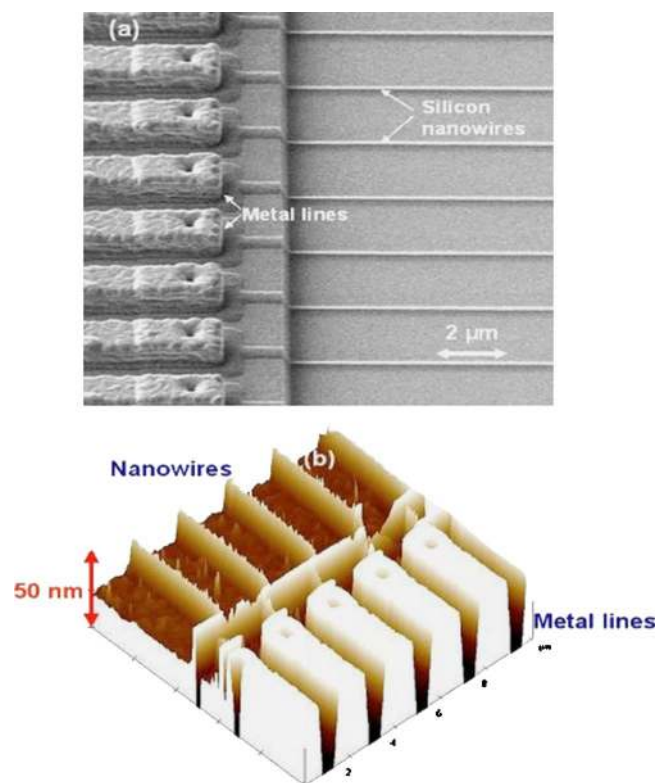
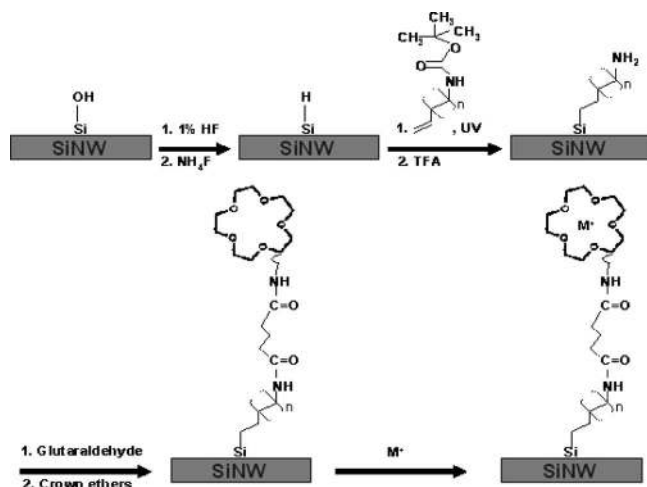


FIG. 1. CMOS-compatible SiNW device layout. (a) SEM image of silicon nanowire device fabricated in CMOS compatible way; (b) AFM image of the same device.

The procedure used to functionalize the SiNWs is illustrated in Scheme 1. Hydrogen-terminated SiNWs were prepared by etching away the SiO₂ coating in 1% HF for 50 s and NH₄F (Fluka) for 60 s. The SiNWs were then coated with an organic monolayer terminated with amine, following a literature procedure.^{13,14} To covalently immobilize the crown ethers on the SiNWs, a bifunctional linker, glutaraldehyde (Aldrich), was employed to bind its one end to the amine at the SiNW surface and the other end to the amine-modified crown ether.¹⁵ Crown ether immobilization was carried out as follows: 10 μ L aliquots of 1.0 mM amine-modified crown ethers in methanol, 4'-aminobenzo-15-crown-5 (Aldrich), and 2-aminomethyl-18-crown-6 (Aldrich) were dispensed onto the



SCHEME 1. Schematic illustration of the SiNW sensor.

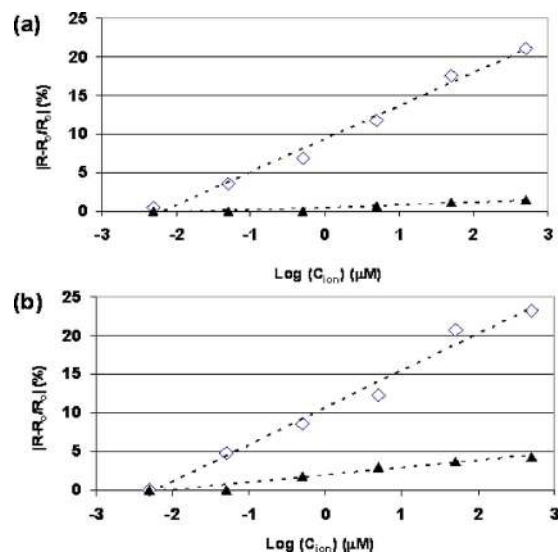


FIG. 2. (a) Response to Na⁺ (\diamond) and K⁺ (\blacktriangle) of the SiNW immobilized with 15-crown-5; (b) response to K⁺ (\diamond) and Na⁺ (\blacktriangle) of the SiNW immobilized with 18-crown-6. R : resistance measured after addition of metal ions; R_0 : resistance measured in the presence of 10 mM TEAC solution.

glutaraldehyde-activated SiNWs and incubated overnight at 20 °C in an environmental chamber. The SiNW were ready to use after a final rinse with water.

Alkali metal ion sensing experiments were performed by monitoring the resistance change of the SiNWs before and after the addition of sample solutions containing the alkali metal ion desired. The SiNW resistance was measured with an Alessi REL-6100 probe station (Cascade Microtech, Beaverton, OR). An aliquot of 2 μ L of 10 mM tetraethylammonium chloride (TEAC) (Fluka) in water was used as blank electrolyte solution to generate a background of the SiNW sensor. Aliquots of 2 μ L of the TEAC solution containing the alkali metal ion of varying concentrations were subsequently injected into the TEAC solution and the resistance was recorded again after it reached the steady state. In the experiments, a fresh SiNW sensor was used for each individual measurement. A mean of the resistance measured simultaneously by an array of the SiNW sensors was utilized for data analysis.

Figure 2 shows the responses of the SiNW sensors to Na⁺ by complexation with 15-crown-5 and K⁺ by complexation with 18-crown-6. Negligible resistance changes were observed in the TEAC solution of different concentrations, indicating that there is no significant buildup of charges at the SiNW surface through electrostatic and nonspecific adsorption. On the contrary, when the SiNW sensors were treated with the metal ions at different concentrations, distinct changes were immediately visible. Figures 2(a) and 2(b) illustrate the dependence of the SiNW resistance change on the concentrations of Na⁺ and K⁺, respectively. Data recorded from 15-crown-5 modified SiNWs showed an \sim 21% drop in the resistance upon the addition of 500 μ M NaCl solution [Fig. 2(a)]. More importantly, a linear relationship between Na⁺ concentration and resistance change was observed from nano- to millimolar. Similar results were obtained for the 18-crown-6-functionalized SiNW to K⁺. Control experiments in which blank SiNWs were employed did not show any appreciable resistance change when 500 μ M NaCl solution or 500 μ M KCl solution was added (data not shown), indicating that the 15-crown-5 and 18-crown-6 are

TABLE I. Ionic diameters and cavity sizes (Ref. 17).

Cation	Ionic diameter (Å)	Crown ether	Cavity size (Å)
Na ⁺	1.94	15-crown-5	1.7–2.2
K ⁺	2.66	18-crown-6	2.6–3.2

essential for Na⁺ and K⁺ detection, respectively. Moreover, the resistance change observed by the two crown ether–modified SiNW sensors is ultrasensitive, achieving a detect limit down to tens of nanomolar level, which is more than three orders of magnitude lower than that of conventional crown ether–based ISEs for Na⁺ and K⁺.¹⁶ These results suggest that complexation of the alkali metal ion at the SiNW surface is responsible for the observed change in resistance. Complexation of the alkali metal ion to the surface immobilized crown ether creates a high density of positive charges on the SiNW surface, providing an electrostatic gating effect (field effect) on the SiNW, which in turn increases the carrier concentration in the *n*-type SiNW, resulting in the observed decrease in resistance. This effect is consistent with those previously noted on other semiconductor nanowire devices,¹ and is essentially the mechanism of semiconductor nanowire sensors.^{4–6}

Crown ethers are known for their unique abilities of selectively forming stable complexes with alkali metal ions and correlate with the close fit of the cation to the crown cavity. Cavity sizes of 15-crown-5 and 18-crown-6 and ionic diameters of Na⁺ and K⁺ are listed in Table I.¹⁷ Clearly, 15-crown-5 selectively complexes with Na⁺ since Na⁺ has the ionic diameter matching perfectly the cavity size. Likewise, 18-crown-6 strongly binds to K⁺ based on the good match of K⁺ ionic diameter to the cavity size of 18-crown-6. On the other hand, TEAC, employed in this experiment as a blank electrolyte solution, has little chance of forming a complex with either of the two crown ethers due to its bulky size.

To establish the selectivity of the SiNW sensor, the Na⁺ sensor, 15-crown-5-functionalized SiNW, was utilized to sense K⁺ and vice versa. Figure 2(a) shows that there was barely any response at different KCl concentrations varying from 500 μM to 50 nM. It is likely that the ionic diameter of K⁺ is much larger than the cavity size of 15-crown-5 and the selectivity of 15-crown-5 to Na⁺ is much better than that of K⁺, which is in good agreement with the reported results.¹⁸ These results demonstrate again that the response of 15-crown-5 to Na⁺ is exactly caused by formation of 15-crown-5-Na⁺ complex of Na⁺ and the SiNW sensor is highly selective. Interestingly, as seen in Fig. 2(b), there was some response of the K⁺ sensor, 18-crown-6 coated SiNW, to Na⁺, but to a much lesser extent. For example, at 500 μM Na⁺, an ~4% resistance drop was observed and it became negligible when the Na⁺ concentration was lower. The selectivities of the 15-crown-5-functionalized SiNW to Na⁺ over K⁺ and the 18-crown-6-functionalized SiNW to K⁺ over Na⁺ were estimated from their responses to these two ions. As shown in Fig. 2, there was a 1.5% resistance change upon the addition

of 500 μM KCl solution to the 15-crown-5-functionalized SiNW, equivalent to that of 15 nM NaCl, implying that the 15-crown-5-functionalized SiNW is approximately 3 × 10⁴ times more selective to Na⁺ than K⁺, whereas, it was 1.0 × 10⁴ more selective to K⁺ than Na⁺ for the 18-crown-6-functionalized SiNW. This is attributable to a much lower stability constant of 18-crown-6-Na⁺ complex (log *K*_s=0.8) than 18-crown-6-K⁺ complex (log *K*_s=2.03), since now Na⁺ is too small for 18-crown-6 and it is only loosely bonded to it.¹⁷

The reproducibility is a very significant issue to sensors. Our device contains 100 parallel SiNWs on one chip. The relative standard derivation of the hundred SiNWs was found to be <3%, showing a very low variation. Furthermore, metal ions were monitored using various crown ether–functionalized SiNW devices under the same conditions. It was found that the relative standard derivation of the device was <10%, which demonstrates a satisfactory reproducibility for such a highly sensitive detection of alkali metal ions using our CMOS-compatible SiNWs.

In summary, we have demonstrated that CMOS-compatible SiNWs functionalized with two crown ethers could function as ultrasensitive alkali metal ion sensors. The SiNW sensors are much more sensitive than conventional alkali metal ion ISEs. Excellent selectivities were also observed. We believe that it is possible to extend this approach to detecting other metal ions and to develop the CMOS SiNW sensor arrays for clinical diagnostic applications.

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