



Oligopeptide-modified silicon nanowire arrays as multichannel metal ion sensors

Xinyan Bi^{a,b}, Ajay Agarwal^a, Kun-Lin Yang^{b,*}

^a Institute of Microelectronics, A*STAR (Agency for Science, Technology, and Research), 11 Science Park Road, Science Park II, Singapore 117685, Singapore

^b Department of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 117576, Singapore

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ABSTRACT

Semiconducting nanowires have the potential to function as highly sensitive and selective sensors for label-free detection of biological and chemical species. In this paper, we describe the preparation and applications of oligopeptide-modified single crystal silicon nanowire (SiNW) arrays as multichannel metal ion sensors. Because these SiNW arrays were fabricated by using a “top-down” process, a very high density of individually addressable SiNW (180 SiNWs grouped into 36 clusters) can be manufactured on a single chip. Furthermore, after two different SiNW clusters are modified with Pb²⁺-selective and Cu²⁺-selective oligopeptide, respectively, concentrations of Pb²⁺ and Cu²⁺ in aqueous solutions can be detected simultaneously and selectively in two different channels. By using the SiNW arrays, we successfully achieved a detection limit of 1 nM for Pb²⁺ and 10 nM for Cu²⁺, respectively. These results demonstrate the potential utility of oligopeptide-modified SiNW arrays for highly sensitive and selective chemical and biological sensing applications.

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1. Introduction

In recent years, more and more examples have demonstrated the potential utility of silicon nanowires (SiNWs) as ultrasensitive and real-time sensors for the detection of metal ions (Cui et al., 2001), small molecules (Wang et al., 2005), viruses (Patolsky et al., 2004), cells (Tang et al., 2005), DNA (Bunimovich et al., 2006; Li et al., 2004, 2005a,b; Hahn and Lieber, 2004; Zhang et al., 2008; Gao et al., 2007), and proteins (Stern et al., 2007; Li et al., 2005a,b; Kim et al., 2007; Zheng et al., 2005). Currently, most SiNW sensors reported in the literatures are fabricated either by using “bottom-up” or “top-down” methods. In the former, SiNWs were synthesized in bulk, and one of the SiNWs was selected and connected to metallic contacts. However, it is often difficult to fabricate a SiNW sensor array with multiple channels following this method because the integration process is quite complicated. In contrast, the “top-down” method permits the production of hundreds of identical SiNWs in an array format. Therefore, each SiNW can serve as an individual sensor which can respond to its own target analyte. Although such a SiNW-based multichannel sensor array fabricated by “top-down” approach shows great promise, to the best of our knowledge, it has not been demonstrated in the literatures before. Most of the SiNW sensor array reported so far, can only respond to one kind of target, such as calcium or copper ion (Bi et al., 2008a,b) or DNA target (Li et al., 2004, 2005a,b). One of the major challenges is the lack of a

suitable sensitive layer which exhibits high specificity for its target. At the same time, the sensitive layer must be thin enough such that the induced electric field can be detected by the SiNW.

Detecting multiple metal ions and quantifying their concentrations in aqueous solutions in a real-time manner is an important analytical problem. Although ion-selective electrodes are readily available for detecting specific metal ions, they can only detect one type of metal ion, and they are difficult to be miniaturized. On the other hand, atomic adsorption spectrometry (Bannon et al., 1994; Parsons and Slavin, 1993; Tahan et al., 1994) and inductively coupled plasma mass spectrometry (Aggarwal et al., 1994; Liu et al., 1999; Bowins and McNutt, 1994) can be used to detect and quantify multiple metal ions simultaneously, but they are not real-time and the instruments are expensive. Considering the limitation of existing technologies in metal ion detection, we exploited oligopeptide-modified SiNW arrays (fabricated by “top-down” approach) for detecting Cu²⁺ and Pb²⁺ simultaneously at two different channels. The high sensitivity, selectivity, small size and fast response makes the SiNW-based sensors an ideal alternative for detecting trace metal ions in water, food and biological samples.

2. Materials and methods

2.1. Chemicals and materials

Lead nitrite, sodium cyanoborohydride (NaBH₃CN), and 4-morpholinoethanesulfonic acid (MES) were purchased from Sigma–Aldrich (Singapore). Pb²⁺-selective oligopeptide (Cys-Asp-Arg-Val-Tyr-Ile-His-Pro-Phe-His-Leu, purity >90%) was synthesized

* Corresponding author. Tel.: +65 6516 6614.

E-mail address: cheyk@nus.edu.sg (K.-L. Yang).

by Research Biolabs (Singapore). Cu^{2+} -selective oligopeptide (Gly-Gly-His) was purchased from Bachem (Switzerland). Triethoxysilane aldehyde (TEA) was purchased from United Chemical Technologies (USA). Oligopeptide solutions were prepared in sodium phosphate buffer (100 mM, pH 7.0) or sodium carbonate buffer (100 mM, pH 10.0). All solvents used in this study were HPLC grades. Water was purified by using a Milli-Q system (Millipore, USA).

2.2. Sensor fabrication and surface modification

Silicon-on-insulator wafers, which have 50 nm thick silicon oxide and 80 nm thick silicon, were used as substrates. First, fin structures (150 nm wide) were patterned on the wafers by using standard DUV lithography and reactive ion etching. Then, they were oxidized in dry O_2 at 900°C . After 2–6 h, 40–50 nm wide SiNWs surrounded by 20–50 nm of SiO_2 were formed during a self-limiting oxidation process. Next, the central part of the SiNWs were doped with phosphorous ($\sim 1 \times 10^{18} \text{ cm}^{-3}$) to form *n*-type SiNWs, and both ends (source and drain) were connected to a metal pad (AlSiCu, with 1% silicon and 0.5% copper, on top of a TaN layer). Finally, the entire chip was passivated with silicon nitride (Si_3N_4) except for the active sensor area and metal pads. For a single chip, it usually consists of 36 SiNW clusters, and each cluster has 5 individually addressable SiNWs (Agarwal et al., 2008).

Before surface modifications, the SiNWs were immersed in 0.5% HF for ~ 10 min to remove SiO_2 layers on their surfaces, and then the chip was kept in dry air overnight to obtain fresh native SiO_2 layers on the SiNWs. Subsequently, the SiNWs were immersed in methanolic solutions containing 2% (v/v) of TEA for 2 h to introduce aldehyde groups on the surface. After this, the chips were rinsed with methanol and dried in a vacuum oven (100°C) for 15 min to allow the cross-linking of silanes on the surface. Then, 0.5 μL of sodium phosphate buffer containing 10 μM of Pb^{2+} -selective oligopeptide and 0.5 μL of sodium carbonate buffer containing 10 μM of Cu^{2+} -selective oligopeptide (with 1 mM of NaBH_3CN) were spotted onto two different SiNW clusters, respectively, by using a micropipette. Pb^{2+} -selective oligopeptide was immobilized through a reaction between the N-terminal cysteine of the oligopeptide and a surface aldehyde group (Bi et al., 2008c) while Cu^{2+} -selective oligopeptide was immobilized through a reaction between the N-terminal amine of the oligopeptide and a surface aldehyde group (Bi et al., 2008b). To prevent the evaporation of the oligopeptide solutions, the chip was stored in a sealed and humid chamber at room temperature for 12 h. Finally, the chip was washed with deionized water and blown dry with nitrogen.

2.3. Complexation with metal ions and electrical conductance measurement

First, different concentrations of Pb^{2+} were prepared in 100 mM of MES buffer (adjusted to pH 6.0 with 1 M NaOH). Then, the oligopeptide-modified SiNWs were covered with 10 μL of Pb^{2+} solution. The conductance of each SiNW was measured by using a semiautomatic probe station Alessi REL 6100 (Cascade Microtech, USA) and a semiconductor parameter analyzer (Hewlett Packard 4156 A, USA). Conductance measurements were performed between -0.5 V and 0.5 V with a stepwise increment of 20.0 mV and a compliance of 100 mA. Conductance of a particular SiNW was then calculated from the slope of current–voltage characteristic curve between -0.1 V and 0.1 V.

2.4. Surface characterization

The microscopic features of SiNWs were observed with a field-emission scanning electron microscope (FESEM, model: JSM-

6700F) from JEOL (Japan). Surface chemical compositions on the SiNWs were analyzed with an energy dispersive X-ray (EDX) attachment.

3. Results and discussion

To obtain good reproducibility in our experiments, a current–voltage (I – V) curve for each SiNW was obtained before any surface modifications were performed. SiNWs which did not give linear I – V curves were discarded. Fig. 1 shows a linear I – V curve for 5 SiNWs in a cluster, suggesting that the electrical contacts are ohmic. Fig. 1 also shows that the 5 SiNWs exhibit slightly different intrinsic conductance. Therefore, we used an average conductance of 15 SiNWs (from 3 different clusters) to minimize the experimental errors in the following experiments.

Fig. 2a shows an optical image of 3 SiNW clusters (100 μM long for each) on a chip. The surface of the first SiNW cluster was modified with Cys-Asp-Arg-Val-Tyr-Ile-His-Pro-Phe-His-Leu, which is a Pb^{2+} -selective oligopeptide (Hu and Loo, 1995; Loo et al., 1994) and the second SiNW cluster was modified with Gly-Gly-His, a Cu^{2+} -selective oligopeptide (Yang et al., 2001). The last cluster was not modified with oligopeptides such that its surface remained aldehyde-terminated. The schematic of the immobilization procedure is shown in Fig. 2b. Thereafter, we immersed these SiNW clusters in a solution containing 100 nM Pb^{2+} and 100 nM Cu^{2+} . After rinsing and drying, SEM–EDX was employed to characterize the surface. Fig. 3 shows that only Pb was detected on the first SiNW cluster modified with Cys-Asp-Arg-Val-Tyr-Ile-His-Pro-Phe-His-Leu while only Cu was detected on the second SiNW cluster modified with Gly-Gly-His. These results suggest that the oligopeptides binds metal ions with high selectivity. We can also conclude that Cys-Asp-Arg-Val-Tyr-Ile-His-Pro-Phe-His-Leu binds Pb^{2+} more strongly than Cu^{2+} while Gly-Gly-His binds Cu^{2+} more strongly than Pb^{2+} . The high selectivity of Cys-Asp-Arg-Val-Tyr-Ile-His-Pro-Phe-His-Leu for Pb^{2+} is probably because Pb^{2+} complexes with one of the His residues and two adjacent carbonyl groups. Another possible mechanism is that both His7 and His10 are responsible for complex with Pb^{2+} (Hu and Loo, 1995; Loo et al., 1994). Similarly, the high selectivity of Gly-Gly-His for Cu^{2+} can be attributed to the formation of three fused chelate rings and a flat 4N coordination plane around Cu^{2+} (Bi and Yang, 2007).

Then, we monitored the conductance of each SiNW in these clusters when aqueous solutions containing different concentrations of Pb^{2+} or Cu^{2+} were delivered to the chip. As shown in Fig. 4, after the injection of 1 nM Pb^{2+} , the conductance of SiNW modified with Cys-Asp-Arg-Val-Tyr-Ile-His-Pro-Phe-His-Leu increases by 5 nS within few seconds and then remains stable, whereas the conductance

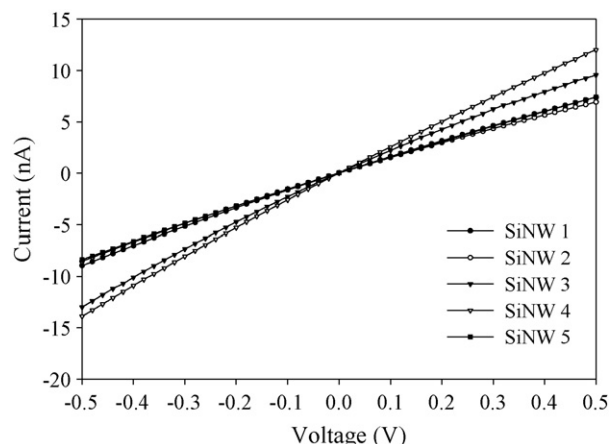


Fig. 1. Typical I – V curves for 5 different SiNWs in one cluster.

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