



Surface composition and interactions of mobile charges with immobilized molecules on polycrystalline silicon nanowires

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ABSTRACT

The polycrystalline silicon nanowire field-effect transistor (poly-SiNW FET) is one of the most sensitive sensors used in real-time and label-free biosensing applications. Its low power requirement, mass production potential, and integrability with electronic components make it a highly attractive device in the rapidly growing diagnostic research field. From the viewpoint of device physics, the charges in the vicinity of a nanowire (NW) surface modulate the electrical characteristics of the NW device. The charges can originate from surface molecules or an ionic solution, and their role in NW biosensing systems remains to be clarified. Determining their role is crucial for understanding the physical interactions of charges in a biosensing event and for the realization of NW-based biosensors. Therefore, using poly-SiNW FET, we investigated the interactions of the immobilized molecules on the NW surface with the mobile charges in solutions. We also investigated the interactions between the mobile charged polymers and the immobilized molecules on the NW surface, and we observed the effect of charge neutrality, originating from Coulomb charge–charge interactions, on the NW conductance. Finally, the isoelectric points between native and sulfated PSGL-1 peptides on the NW surface were identified. This study provides a physical understanding of the charge–charge interaction of mobile charges with immobilized charged molecules on a nanoscale surface and presents new opportunities for using charge-based detection in biological and chemical sensing applications.

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1. Introduction

The poly-crystalline silicon nanowire field-effect transistor (poly-SiNW FET) is one of the most sensitive sensors used in real-time and label-free biosensing applications. Many silicon nanowire field-effect transistor base biosensors have been developed for the ultra-high detection of a variety of proteins, nucleic acids and small molecules [1–9]. Its low power requirement, mass production potential, and integrability with other electronic

components make the poly-SiNW FET a highly attractive device in the fast-growing diagnostic industry. However, challenges remain due to grain boundary associated complexity and difficulty in processing of ultra-thin nanowires in spacer etch process for single molecular level detection. A field-effect transistor (FET) sensor has the structure of a common three-electrode transistor; the source and drain electrodes bridge the semiconductor channel and the gate electrode modulates the channel conductance [10]. In the case of poly-SiNW FET-based sensors, the semiconductor channel is made of polycrystalline silicon (poly-Si) and is used as the sensing component. The NW electric properties are dependent on its surrounding interface, which makes NW nanomaterials excellent substrates for molecular sensing applications. The use of poly-SiNW FETs for biosensing depends on the variation of charges surrounding the nanowire (NW) surface, which can modulate the electrical characteristics of the NW device, implying that the surface properties of the NW play a crucial role in determining the electrical characteristics of NW FET devices.

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Few studies have been devoted to understand the mechanism of how surface properties of poly-SiNW can modulate the electrical characteristics of a poly-SiNW FET. Investigations on single-crystalline NW FET indicate that the surface molecules play a critical role in determining the physical, chemical, and electrical characteristics of the NWs [11–14]. The NW FET devices directly detect the NW surface charge on the exposed gate dielectric surface. Study on SnO₂ nanobelt FETs indicates that surface charges cause local interfacial potential changes over the gate dielectric, which alter the channel conductance, and the signal output is produced [15]. Poly-SiNW surface may exhibit similar or different phenomena as those described above by single-crystalline and SnO₂ materials. Key features of the NW FET include the capability to perform local measurements with considerably high sensitivity for generating an electric response to the NW surface charge. Previous studies have revealed that NW biosensors are highly sensitive to its pH environments because of the ionization state of the NW surface varied under various pH conditions [14–17]. Surface modifications on NW surface can extensively affect the electric responses of the NW biosensors that usually require specific probes on sensing surface to recognize specific targets. In addition, various pH buffer solutions can also have distinct ionic strengths, which is another variable to affect sensing results. The relationships among the solution ionic strength, pH value, and surface composition of the NW in the NW biosensor remain unclear and need to be further characterized.

In this study, we investigated interactions between the channel (poly-SiNW) surface and solutes on the NW sensing area, which is one of the most critical steps in biosensing. The pH effect was conducted with sodium phosphate buffered solutions by using an integrated microfluidic system on the NW. The responses of the channel conductance to pH values were measured at distinct gate voltages, and the poly-SiNW biosensor with the highest sensitivity was observed when we operated the device in the subthreshold regime while applying an appropriate voltage at the liquid gate. Four types of functional group were prepared on the poly-SiNW surface, and they were used to assess the correlation of the ionization state-specific mapping of functional group distributions on the NW surface. The pH-dependent changes in the electric response of the surface charge were exploited to map the changes in the ionization state on the NW surfaces upon the addition of the charged polymers. In addition, tyrosine sulfation of P-selectin glycoprotein ligand-1 (PSGL-1), which has been used to regulate physiological functions and pathological diseases through sulfated protein–protein interactions [18,19], was selected to approve the concept in the presence of a biological molecule. Sulfation of PSGL-1 is critical for invasion of PSGL-1 by specific strains of enterovirus and for the surveillance of enterovirus 71 strains that cause severe neurological diseases [20], in which the capsid protein of the virus strains interacts with sulfated PSGL-1 to invade a host cell [19]. The tyrosine sulfation of PSGL-1 can be detected by analyzing the pH profile of the functionalized poly-SiNW biosensor.

Our observation implies that the ionic strength, pH value and modified sensing surface are crucial variants in a biosensing environment. It has been well established that all biochemical interaction occurs under suitable pH and ionic environment. Thus, it is important to find the balance between high Debye length (need low ion concentration) and high salt environment for detection of biomolecular interactions such as DNA–DNA, protein–protein or protein–DNA interactions. Our results indicated that at low buffer concentration poly-SiNW FET response may suffer from instability and at high buffer concentration it becomes stable. This should be applicable for any immobilized analytes on NW surface whether it is protein, DNA or any other biomarker for the particular platform presented. This study provides several useful methods for

optimizing the sensor performance for chemical and biomolecular detection in the future.

2. Materials and methods

2.1. Materials

3-Aminopropyltriethoxysilane (APTES), glutaraldehyde, propyltrimethoxysilane (PTMS), polyallylamine hydrochloride (PAH), polysodium 4-styrenesulfonate (PSS), sodium cyanoborohydride, succinic anhydride (SA), and tris(hydroxymethyl) aminomethane were purchased from Sigma–Aldrich (USA). Sodium carbonate (SC) was purchased from Riedel-de Haën (Germany). Sodium phosphate monobasic and sodium phosphate dibasic were purchased from J.T. Baker (USA). PSGL-1 peptide (ATEYEYLDYDFL) and sulfated peptide were purchased from Genemed Synthesis, Inc. (USA) and Kelowna International Scientific, Inc. (Taiwan), respectively. All reagent solutions were prepared with DIW (water resistance was 18.2 MΩ cm) from an ultra-pure water system (Millipore).

2.2. Fabrication of poly-SiNW FET devices

Poly-SiNW FET devices were fabricated using process facilities at the National Nano Device Laboratories (Hsinchu, Taiwan). An n-type field-effect transistor, comprising two poly-SiNWs that served as conducting channels and that had dimensions of 100 nm width and 1.6 μm length, was fabricated using the sidewall spacer technique [4–7,21–24]. This technique is compatible with current commercial semiconductor process technologies and has been developed by our team, with an emphasis on applications in aqueous solutions [3–7,22–25].

2.3. Functionalization of the device surface

Amino-terminal modification of the poly-SiNW surface was performed by following a one-step procedure, as illustrated in Fig. 1. The device was first washed with pure acetone and ethanol for 5 min to remove contaminants and then immersed in a 2.0% APTES/ethanol solution for 30 min to introduce amino groups on the poly-SiNW surface. The device was cleaned with pure ethanol (99.5%) three times and blow-dried with nitrogen gas to remove the unbound APTES molecules, which was followed by bake-drying at 120 °C for 10 min to remove the surplus ethanol. A carboxylic surface was prepared by immersing the amino-terminal device in 1.0 wt% SA in a 100 mM sodium carbonate for 4 h. NW FETs with a hydrophobic methyl terminal were prepared using a similar procedure; however, a 2.0% PTMS/ethanol solution was used in place of the APTES/ethanol solution. The device was then cleaned with the Na-PB and blow-dried with nitrogen gas. Furthermore, PSGL-1 peptides were immobilized on a poly-SiNW surface by following a three-step procedure. An APTES-modified device was obtained using the aforementioned procedure, and the device surface was subsequently immersed in solutions of 12.5% glutaraldehyde in 10 mM Na-PB (pH 7.0) for 1 h followed by a Na-PB wash. Finally, 10 μM PSGL-1 peptides were coupled to the surface of the NWs in Na-PB overnight. Unreacted aldehyde groups were blocked through mixing with a 10 mM Tris buffer (pH 7.0) containing 4 mM sodium cyanoborohydride for 10 min, and the modified poly-SiNWs were washed with 10 mM Na-PB (pH 7.0).

2.4. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) surface analysis was performed using a Thermo Fisher Scientific Theta Probe system with a monochromatic Al Kα X-ray source (1486.6 eV) and a concentric hemispherical analyzer. High-resolution spectra (C1s and

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