Biosensors based on nanowire field effect transistors with Schottky contacts

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Abstract. A top-down nanofabrication approach was used to obtain silicon nanowires from silicon-on-insulator wafers using direct-write electron beam lithography and plasma-reactive ion etching. Fabricated with designed pattern silicon nanowires are 0.4, 0.8, 2 µm in width and 100 nm in height. The devices can be applied in future medical diagnostic applications as novel biosensors with detection principle based on the changes in electrical characteristics of the silicon nanowires functionalized with thiol-containing molecules.

1. Introduction

Nanometer-scale structures, in particularly silicon nanowires (NW), attract considerable attention due to their possible application in nanotechnology and nanomedicine since their sizes are comparable to the sizes of chemical and biological species for detection. At that time in integrated nanoscale electronics the considerable attention is also paid to devices based on Si NWs with Schottky contacts [1,2]. In a point of fact, Schottky barrier FETs are of great interest on their own account as an alternative to traditional doped source and drain device structures, because sub-100 nm ranges scaling encounters fundamental problems including high leakage current and parasitic resistance. Many research groups have demonstrated different methods for the implementation of such devices in a nanoscale [3-8]. The sensing mechanism of such devices may be described in terms of the change in charge density, which induces a change in the electric field at the silicon nanowire surface. The most important applications of the SiNW FET biosensor are in disease diagnosis using specific probe molecules for nanowire functionalization these devices may operate as selective sensors for detection of nucleic acids [9], proteins [10], protein-DNA interactions [11], cells [12], and viruses [13]. The most popular method for fabrication of such devices in nanoscale is “top-down” synthesis approach [14-19], which allow to regulate device geometry and electrical characteristics due to precise control of lateral sizes of nanowire and enables direct contact with other structures on device. In comparison with “bottom-up” approach which usually use chemical methods to obtain nanostructures [20, 21] which are incapable to control geometrical characteristics. Taking into account the advantages of “top-down” approach, we report nanofabrication technology of biosensor based on Schottky barrier nanowire FET using electron beam lithography (EBL) process and chemical wet and plasma-reactive ion etching (RIE), the functionalization process of nanowire surface using the tip of atomic-force microscope and the results of thiol molecules detection.
2. Materials and methods
SiNW sensors are typical FET-based devices with Schottky contacts and have a number of advantages including good suppression of short channel effects, simple and low temperature processing and the elimination of doping and subsequent activation steps. These features are particularly desirable for SiNW devices because they can circumvent difficult fabrication issues such as an accurate control of the doping type and the formation of reliable ohmic contacts. SiNW FET sensors include source, drain and gate electrodes connected with the semiconductor nanowire, which serves as the sensing component of the device. Nanofabrication technology of silicon nanowires (nanowire FET) using “top-down” approach represents a multistep process, which will be briefly described in this paper.

2.1. Fabrication of biosensors based on SiNW FETs
Silicon nanowires were fabricated from SOI (100) wafers with 200 nm of the buried oxide (BOX) and 100-nm monocrystalline top boron doped silicon layer (with resistivity of 18 Ω·cm). Firstly, the SOI wafer was cleaned to remove contaminants and native oxide. After the cleaning procedure, thermal evaporation in ultra-high vacuum was used to obtain the thin film of Fe and then the EBL process was used to obtain Fe contact pads to allow the carrying out of the investigations of the electric properties. The metal contact pads for the source (S) and drain (D) were connected to each end of the fabricated nanowire. Further, the positive tone resist was spin coated on the sample and dehydrated on a hotplate. The next step was the EBL exposure process, after the sample was treated in nitric acid solution for etching of Fe film in areas not covered with the photoresist. Then reactive ion etching (RIE) was used with the help of NORDSON MARCH RIE-1701 plasma system to etch Si film. The result of described technological process is an array of silicon nanowire structures on a dielectric layer with metal pads for the source (S) and drain (D) connected to each end of the fabricated nanowire and allow to carry out the measurements of the electrical properties. In addition, besides of the metal pads in the fabricated structure a back gate was obtained on the backside of the SOI substrate using doping with indium (In). A top view SEM image of the silicon nanowires after the dry etch process is shown in Fig 1(a). The results indicate that the silicon nanowires were formed with good uniformity, high resolution and good pattern placement. AFM images show the width of the silicon nanowires are correspondingly 0.4, 0.8, 2 µm Fig 1(b, c, d).

Figure 1. (a) SEM and (b, c, d) AFM images of fabricated devices with nanowire 0.4, 0.8, 2 µm in width correspondingly.

2.2. Nanowire functionalization
Functionalization of the silicon nanowire surface with a probe molecule is necessary step to evaluate the performance of manufactured devices. There are two approaches to attach the detectable molecule on the surface of silicon nanowire: electrostatic adsorption and covalent binding [22]. Electrostatic adsorption uses the attractive force responsible for adsorbing ionic solute on an oppositely charged adsorbent. In our case there is the coordinate covalent bond, which is based on the charge transfer between the probe molecule and SiNW surface molecules without the formation of a chemical bond. Since oxide can grow on the SiNW surface naturally, a number of methods rely on the functionalization of the oxide layer [23, 24]. For this purpose, the organic polymer 1-octadecanethiol (ODT) dissolved in
acetonitrile was deposited on the nanowire surface [25]. This polymer is CH$_3$-(CH$_2$)$_{17}$-SH compound, where the first part (CH$_3$-(CH$_2$)$_{17}$) is organic substituent and the second part (SH) is the positively charged thiol group, which binds with the nanowire surface [26]. Using the probe of atomic-force microscope it is possible to deposit molecules on surface through the diffusion of particles through a water meniscus connecting the probe and the substrate (Fig. 2(a)). The environmental conditions during the experiment were supported with environment control chamber, so the temperature was stable at 24 - 26°C and relative humidity was about 44 - 49%. When the detectable molecules are deposited on the nanowire surface they start to form self-assembled layer due to Van der Waals interactions, [27] as a result reducing its own free energy (Fig. 2(b)) [28]. Changes occurring between the ODT molecules and the silicon surface were converted into an electrical signal. This signal was measured with the help of a probe station Lakeshore EMPX-HF 2 and Keithley 2634b SourceMeter at room temperature for pure nanowire and with deposited ODT-molecules.

3. Results and discussions
The quality of fabricated devices especially silicon nanowires is characterized by measuring of transfer characteristics with various source-drain bias $V_{SD}$. These characteristics demonstrates device current changing during gate voltage sweep for 0.4 µm nanowire in Fig. 2(c).

![Figure 2](image)

**Figure 2.** (a) Image of ODT-molecules deposition on the nanowire surface using AFM probe. (b) Scheme of ODT-molecular configuration. (c) Transfer characteristics of a SiNW FET with a nanowire width of 0.4 µm at different drain-source voltages for a pure nanowire and nanowire with deposited ODT. (d) Detection sensitivity for 400 nm nanowire at different biases at the back gate.

It is noted that the deposition of ODT-molecules does only the shift of transfer characteristic towards positive bias, herein the shape of the graph is almost unchanged. Thus, it is expected that the ODT-molecules don’t influence on the operating modes in radical way that means main physical mechanisms of charge...
carrier transport in nanowires remain the same. The influence of ODT-molecules on the transport in nanowire may be considered as the enabling of an effective additional bias voltage at the gate or, that is more logically, as an appearing of virtual top gate. As shown in paper of Naumova et al [29] the shift of transfer characteristics towards higher positive bias may be caused by negative surface-charge density in silicon nanowire that is possible at the positive bias on the top gate. In our case ODT-molecule represents as a compound with positively charged thiol group able to bind with SiO, that covers nanowire surface. When the detectable ODT-molecule is deposited on the nanowire surface the coordinate covalent bonding appears and, as a result, the negative surface-charge density occurs in silicon nanowire. Thus, ODT-molecules operate as a top field gate of transistor. This result made possibility for electrical detection of organic molecules.

The efficiency represents the ability of fabricated devices to detect. The measurements of their characteristic show that the most sensitive is SiNW FET with 0.4 µm nanowire (Fig. 2(d)). Maximal value of sensitivity is defined as the relative nanowire current change after deposition of ODT-molecule (Sens = 100% · ISD / ISD clean), that is more than 1000%, and is observed at relatively low voltages (VSD=5V, VGD=4V). For nanowires with larger widths the sensitivity roughly decreases. This fact may be caused by area of ODT-molecule deposition, which is tiny in comparison with the surface area of wide nanowires (0.8 and 2 µm). These investigations confirmed that devices fabricated using top-down nanofabrication process are of high quality and have a great potential for further development as biosensors.

4. Conclusions
Top-down approach was used to fabricate biosensors based on Schottky barrier SiNW FETs with different nanowire widths (0.4, 0.8, 2 µm) using multistep process including thermal evaporation in ultra-high vacuum, EBL and RIE processes. The results of SEM and AFM measurements of fabricated devices present good quality of technological process. Electrical investigations, in particular, transfer characteristics of the fabricated SiNW FETs demonstrates device current changing during gate voltage sweep after ODT-molecules deposition that is caused by covalent binding of positively charged thiol part of deposited molecule. Maximal value of sensitivity is defined for nanowire of 0.4 µm in width. According the carried out investigations it is possible to conclude that the fabricated nanowire biosensors have great potential for biomedical diagnostic applications.

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References
[1] Zhang, Guo-Jun, Yong Ning, Analytica Chimica Acta 749, 1.
[2] Thomas Mikolajick, Walter M. Weber, 2015 Anisotropic Nanomaterials, 1-25.
[3] Farahidah Zabah Nor et al. 2012, Journal of Applied Physics, 112.
[4] Vu XT, Ghosh Moulick R et al. 2010, Sensors and Actuators B, 144, 354–360.
[5] Rius G, Llobet J et al. 2011, AIP Conf. Proc, 1336.
[6] Gao A, Lu N et al. 2014, Nanoscale, 6(21), 13036–13042.
[7] Adam Tijjani et al, 2013, African Journal of Biotechnology, 12(36), 5486–5495.
[8] Shaurya Prakash, Junghoon Yeom, 2014, Nanofluids and Microfluidics; In Micro and Nano Technologies: 171–239.
[9] J.-I. Hahm, C.M. Lieber, 2004, Nano Lett., 4, 51–54
[10] G. Zheng, F. Patolsky et al, 2005, Nat. Biotechnol., 23, 1294–1301.
[11] G.-J. Zhang, M. Huang et al., 2010, Biosens. Bioelectron., 26, 365–370.
[12] F. Patolsky, B.P. Timko et al., 2006, Science, 313, 1100–1104
[13] Patolsky, G. Zheng et al., 2004, Proc. Natl. Acad. Sci. U. S. A., 101, 14017–14022.
[14] Chen KI, Li BR, Chen Y., 2011, Nano Today, 6, 131–154.
[15] Park I, Li Z, Pisano AP et al., 2010, Nanotechnology, 21, 1–9.
[16] M.Nuzaihan MN, Hashim U et al., 2015, Current Nanoscience, 11, 239–244.
[17] Teo Boon K, Sun XH, 2006, Journal of Cluster Science, 17(4), 529–540.
[18] Tran DP, Wolfrum B et al., 2014, J. Mater. Chem. C, 2(26): 5229–5234.
[19] Nor MNM, Hashim U et al., 2010, Am. Inst. Phys. Conf. Proc., 1217, 272–278.
[20] Cui Y, Wei Q, Park H et al., 2001, Science, 293, 1289–1292.
[21] Hsiao CY, Lin CH et al., 2009, Biosensors and Bioelectronics, 24, 1223–1229.
[22] Zhang, Guo-Jun, Yong Ning, 2012, Analytica Chimica Acta, 749, 1-15.
[23] G.-J. Zhang, J.H. Chua et al., 2009, Biosens. Bioelectron., 24, 2504–2508.
[24] J. Chua, R.E. Chee et al, 2009, Anal. Chem., 81, 6266–6271.
[25] R. D. Piner, J. Zhu et al., 1999 J. Science 283(5402), 661.
[26] Johannes G. et al., 2003, Interfacial Supramolecular Assemblies. Wiley, 88–94.
[27] Kifer, Angel, 2001, Supramolecular Electrochemistry. Coral Gables. Wiley VCH, 191–193.
[28] Love, J. Christopher, et al., 2005, Chemical reviews, 105, 4, 1103-1170.
[29] Naumova et al., 2010, Sci. Technol. 25, 055004