Novel Fabrication Method of Conductive Polymer Nanowires for Sensor Applications

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ABSTRACT

In this work we demonstrate a new, quick and low cost fabrication of PEDOT:TsO nanowires using self-assembled peptide nanotubes as a masking material. The peptide nanotubes show a remarkably stability during reactive ion etching and can be dissolved in water afterwards. We have shown that the impedance of the nanowire is changing with backgating the wire, this gives promising possibility for application as a sensor.

Keywords: PEDOT:TsO, Nanowire, Self-assembly, Fabrication, Diphenylanaline

1 Introduction

In 2001 the original paper on silicon nanowires demonstrated the potential of these new biosensors [1]. Since then the field has been explored thoroughly [2][3][4]. The largest challenge of utilizing the nanowires as biosensors for diagnostic purposes is the fabrication costs [5]. One of the approaches used to lower the fabrication costs has been to explore cheaper materials as an alternative to silicon. In recent years a lot of work has emerged on conducting polymers such as polyanaline [6][7][8] and PEDOT [9][10][11]. The benefits of the low cost nanowire devices have been demonstrated in various applications ranging from chemical gas and liquid sensors [12][13] over temperature sensors [14][29] to biosensors [15][16][17]. However, the fabrication processes of these polymer nanowires are proving to be challenging and often time consuming. Recently we have demonstrated the use of self-organizing diphenylanaline peptide nanotubes (PNT's) as masking material for reactive ion etching (RIE). This has given rise to low cost, rapid and mild clean room fabrication of silicon nanowire devices [19][20]. Diphenylalanine self-assembled peptide nanostructures are biological entities that self-organize in rapidly under mild conditions. Its on-chip fabrication, structural and electrical characterization, manipulation and application in the development of biosensors were recently reported [21][22][23][24][25]. In this work we have demonstrated the rapid fabrication of PEDOT:TsO nanowire devices based on PNT masking for RIE etching.

2 Materials and Methods

2.1 Chemicals

Lyophilized diphenylalanine dipeptide powder was acquired from Bachem (product number: G-2925). All other chemicals utilized were acquired from Sigma-Aldrich.

2.2 Backgate electrode

To be able to backgate the nanowires the SiO_2 layer on the backside of the wafer was stripped by 5 min. in buffered hydrofluoric acid. Followed by sputtering on a 100nm Al layer.

2.3 Gold Electrode Patterning

Gold contact electrodes were fabricated by sputtering 10nm Ti and 90nm Au onto a Si wafer with a 500nm SiO_2 on top. The electrodes were patterned using standard lift-off process.

2.4 PEDOT:TsO Preparation

2.6 ml Baytron C (40,% $Fe^{(III)}$tosylate in butanol), 800 μl butanol, 60 μl pyridine and 70.5 mg EDOT-OH were thoroughly mixed and spun on the substrate wafer with 4000 rpm for 60 s. The coated wafers were heated to 70C for 10 minutes to evaporate the inhibitor pyridine and start the polymerization process. The wafers were finally rinsed in de-ionised water to wash away excess reactants. This procedure ensures a PEDOT:TsO film thickness of 75 nm.

2.5 Preparation of Diphenylalanine Peptide Nanotubes

The PNT's were prepared from a stock solution. Lyophilized peptide monomers were dissolved at a concentration of 100 mg/ml in 1,1,1,3,3,3 hexaflouro-2-propanol (HFP). The HFP stock solution was diluted to a final peptide concentration of 2 mg/ml in water in which process the PNT's forme. Fresh stock solution was prepared prior to experiments to avoid pre-aggregates.

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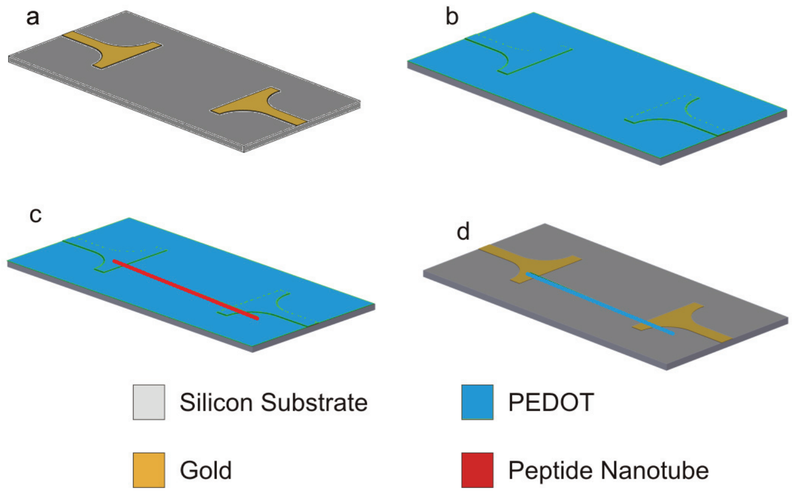

Figure 1: Illustration of fabrication process. Initially a 500nm SiO_2 layer is grown on a Si wafer. Then the Au electrodes are patterned using a lift-off procedure. Then the PEDOT:TsO is spin coated on top. Then the PNT's are spin casted on the coated wafer. For transfering the PNT's pattern to the PEDOT:TsO the wafer is etched using reactive ion etching. Finally, the PNT's are dissolved in Milli Q water. The entire process can be concluded in approximately 5 hours.

2.6 Spin Casting Procedure

The PNT's were positioned across the electrodes using a spin casting procedure described in [20]. Freshly prepared peptide solution containing the newly formed PNT's is added in individual drops onto the center of a spinning substrate. The spinning forces the PNT's to align radially on the surface of the wafer.

2.7 Reactive Ion Etching Procedure

The PEDOT:TsO was patterned using reactive ion etching (STS Cluster System C010) with a pressure of 300mTorr and a power of 100W. An oxygen based plasma was used (98 SCCM O2 and 20 SCCM N2) for 15 s, which was enough to etch through the thin PEDOT:TsO layer.

2.8 Visualization

All scanning electron microscopic (SEM) images were acquired using a Zeiss supra 40 VP operated in the in-lens mode with an acceleration voltage of 3 kV. The atomic force microscopy (AFM) measurements were conducted using a PSIA XE 150 in both tapping (for topography imaging) and contact (for conductive recordings with a tip bias of 0.7 V) mode. The conductive AFM images were acquired with a Cr/Pt coated cantilever (ContE-Al, Budget Sensors) with a force constant of 0.3 mN. The current between the AFM tip and sample was measured using an inverting current amplifier and one of the analogue-digital converter inputs of the AFM controller.

2.9 Electrical Readout

The impedance of the PEDOT:TsO nanowire device was recorded with a custom build lab view controlled experimental setup, where the current through the PEDOT:TsO nanowire is externally amplified using a low-noise current preamplifier model: SR570 from Stanford Research Systems and finally recorded using a National Instruments data acquisition card model BNC-2111.

3 Results and Discussion

3.1 Fabrication of PEDOT Nanowires

We have previously showed the use diphenylanaline PNT's as masking material for dry etching of silicon nanowires [19][20]. In this work we present a modified version of the fabrication process where we utilize the PNT's masking ability to make a rapid and low cost fabrication of PEDOT:TsO nanowire devices. Following this process it is possible to fabricate around 200 PEDOT:TsO devices in approximately 5 hours. In figure 1 the fabrication process i scheduled (not including the back gating electrode). The first and most time consuming part of the fabrication is to insulate the Si wafer from the electrodes and pattern the electrodes. The first is done by growing 500 nm SiO_2 layer from bare silicon. The later is done by a standard lift-off process after depositing 10 nm Ti as an adhesion layer followed by de-

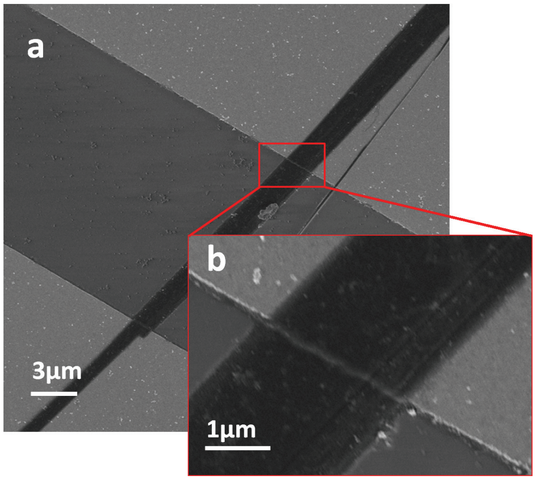

Figure 2: A SEM image of a PEDOT:TsO bridging two Au electrodes is shown in a. b shows a zoom of the contact between the Au and PEDOT:TsO nanowire. It is seen that the step covering is very good.

positing 90 nm Au. The PEDOT:TsO is then spun on top of the patterned electrode. To ensure a height of the PEDOT nanowire of 75 nm a spin rate of 4000 rpm was used. Because the PEDOT:TsO is polymerized directly on the Au the electrical contact between the Au and PEDOT:TsO is very good. The PNT's are then applied onto the substrate one drop at the time at the center of a wafer while spinning, as described in [20]. This ensures that the PNT's align radially from the center of the wafer. By designing the Au electrodes so they are perpendicular to the radial direction it makes it possible for the PNT's to bridge two electrodes. Now using the PNT's across electrodes as etch masks the PEDOT:TsO is patterned using RIE. Finally the PNT's are removed by washing with milli Q water.

3.2 Characterization of PEDOT:TsO nanowires

The fabricated PEDOT:TsO nanowires were characterized by both atomic force microscopy (AFM) and scanning electron microscopy (SEM). A SEM image of the PEDOT:TsO bridging two Au electrodes is shown in figure 2a. Figure 2b shows a close up of contact of the PEDOT:TsO and Au electrodes a very smooth conformity is observed. AFM was used to determine the height of the PEDOT:TsO nanowire to 75nm.

3.3 Electrical Characterization

The very smooth conformity of the PEDOT:TsO to the Au electrodes indicates a very good electrical connection. To investigate this further the current voltage

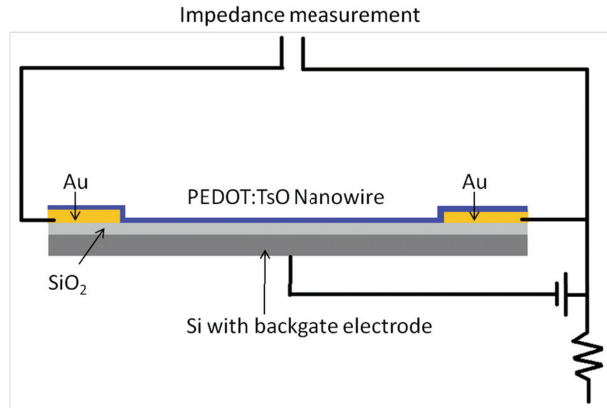

Figure 3: Shows an illustration of the experimental setup. The impedance is measured between the two Au electrodes, while applying a backgate potential.

relationship (IV-curve) of a single PEDOT:TsO nanowire was measured. The IV-curve showed a completely linear response proving that an ohmic electrical contact between the Au eletrodes and PEDOT:TsO nanowire was established. The impedance measurement setup is illustrated in figure 3.

3.4 Backgating Experiment

The traditional silicon nanowire devices functions as a FET. The current is running between the source and drain electrode when applying a gate potential the conductance will either increase or decrease. The conductance dependency on the gate voltage has led to the idea of using FETs for electrical sensing. Imagining a number of charged target molecules attaching to the nanowire, this is analogous to applying a potential using a gate electrode [28]. To demonstrate an initial requirements for using the PEDOT:TsO nanowire as an alternative to the traditional silicon nanowire we were backgating the PEDOT:TsO nanowires. As previously described a backside contact in Al was added to the device. By connecting an external power supply to the backside of the device and to ground the backgating potential could be applied. The potential was applied on and off in steps of 10V from 0V to 60V in time intervals of 1 min. Figure 4 shows that the impedance is increasing linearly with the applied gating potential.

4 Conclusion

In this work we have showed a new and rapid fabrication method of polymer nanowires (Infact the entire fabrication process can be conducted in approximately 5 hours). We have combined bottom up fabrication using self-assembled peptide structures for the patterning of PEDOT:TsO nanowires with top down fabrication of macroscopic gold electrode patterns to provide contact

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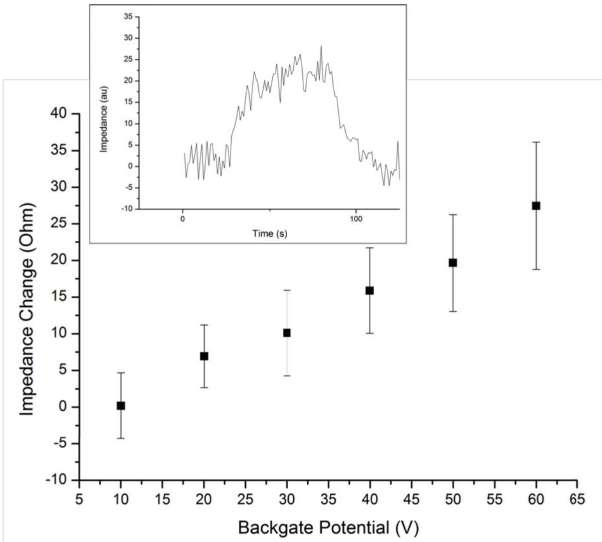

Figure 4: Shows the change in impedance corresponding to an applied a backgate potential. The insert shows an impedance change over time, while a backgate potential of 50V is turned on and off.

pads for electrical contact. We have demonstrated that the impedance of the PEDOT:TsO nanowire is changing when applying a backgate potential.

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