

Synthesis, characterization and application of electroless metal assisted silicon nanowire arrays



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ABSTRACT

Vertically aligned silicon nanowire arrays (SiNWs) have been synthesized by electroless metal deposition process. The fabricated SiNWs have an average diameter of 75 nm and 3.5–4.0 μm length, as confirmed from scanning electron microscopy. A characteristic asymmetric peak broadening at 520 cm^{-1} from Raman spectroscopy was obtained for the SiNWs as compared to the bulk silicon crystal due to phonon confinement. The as-prepared SiNWs exhibit good electron field-emission properties with turn-on field of about $8.26\text{ V }\mu\text{m}^{-1}$ at a current density of $4.9\text{ }\mu\text{A cm}^{-2}$. The SiNWs was functionalized by coating with a thin gold metallic film for 60 s, and then used as bio-probe for the detection of bovine serum albumin (BSA) protein molecules. From the linear sweep voltammetry analysis, the Au coated SiNWs, exhibit linear response to the BSA analyte with increase in concentration. The minimum detection limit of the protein molecule was calculated of about $1.16\text{ }\mu\text{M}$ by the as-synthesized SiNWs probe.

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1. Introduction

Semiconducting nanostructures have captured the attention of a large number of researchers owing to their unique low-dimensional properties that leads to enhanced device performance. Silicon nanowire arrays (SiNWs) are popular because of their importance in microelectronics [1]. SiNWs have a number of potential applications due to their novel physical properties such as light emission [2], electron field emission [3], enhanced thermoelectric performance [4], and quantum confinement effect [5]. Applications of SiNWs include the field effect transistors [6], logic circuits [7], and chemical and biological sensors [8,9]. Chemical sensors and biosensors using SiNWs have attracted wide attention because of their biocompatibility [10], vast surface to volume ratio [11], fast response and good reversibility [8], and oxide coated or H-terminated surface [12], which allows easy attachment of various functional groups.

SiNWs are prepared by different methods such as chemical vapor deposition [13], laser ablation [14], DC arc discharge method [15], thermal evaporation [16], and solution based methods [17]. However, electroless metal deposition (EMD) technique is unique and, cost-effective, operates at ambient conditions, has a fast and easy control on preparing SiNWs of different morphologies [11], and involves wet-chemical etching of silicon substrate in a strong oxidizing environment [18–21]. Here, we report gold (Au) nanoparticles supported silver (Ag) assisted EMD process for synthesizing arrays of SiNWs. The as-prepared SiNWs were further used for field emission studies for possible device applications. Further, a facile coating of Au thin film onto the surface of SiNWs for bovine serum albumin (BSA) protein bio-molecules detection was carried out by electrochemical technique.

2. Experimental details

2.1. Chemicals and materials

All the chemicals used in the experiment were analytical grade and used without further purification for cleaning silicon substrates, preparing SiNWs and electrochemical electrolytes at an ambient condition. High grade n-type silicon substrates of plane (100) were used for synthesis of SiNWs. Phosphate buffer (PBS)

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solutions used in the experiment contained (pH 7.4) 0.1 M KH_2PO_4 , 0.1 M $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ and 0.1 M NaCl.

2.2. Synthesis of SiNWs and its functionalization

A standard RCA process was adopted to clean various organic and metallic impurities from the silicon substrates. Then gold metal ions were sputter on Si substrate surface for about 25 s with help of ion sputter E-1010, Hitachi. The coated sample was heated in argon atmosphere at 1073 K for 3 h and immersed separately in an aqueous solution of 0.103 M AgNO_3 in 12 ml of 48% HF for 30 min. The treated substrates were removed from the solution and washed thoroughly with aqueous nitric acid followed by deionized water. These as-synthesized arrays of SiNWs were used for field emission studies. Further, the SiNWs, coated with Au film by ion sputter for about 60 s were used for electro-analytical studies of BSA protein biomolecules.

2.3. Electrochemical analysis

Electrochemical experiments were performed using a conventional one-compartment three-electrode electrochemical cell. The working electrode (WE) was an Au-coated SiNWs arrays of dimensions 1.0 cm $\times$ 1.5 cm; a platinum wire was employed as the counter electrode and a saturated calomel electrode (SCE) served as the reference electrode. The electrolyte containing 3, 4, 4.5, 5, 5.5, 6 and 7 μM BSA molecules was taken in (pH 7.4) 0.1 M PBS and the linear sweep voltammetry (LSV) analysis were carried out by the potential scan ranging from 0 to 1.4 V with a constant scan rate of 10 mV s^{-1} .

2.4. Characterization

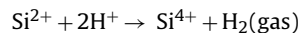
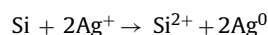
The morphograph and topograph of the as-prepared SiNWs were studied using a scanning electron microscope (SEM) of PHILIPS, XL30 model and atomic force microscope (AFM) of XE70, Park systems, using non-contact model. Raman spectra analyses were performed using 514 Argon ion laser source of wavelength of 514 nm by Jobin Yvon-Horiba T6400 system. Electric field emission (EFE) properties of SiNWs were recorded by Keithley 6512A electrometer in a homemade parallel cathode–anode setup and analyzed by Fowler–Nordheim model. Electrochemical analysis was carried out with electrochemical workstation, CHI 660C, USA model.

3. Results and discussions

3.1. Synthesis of SiNWs

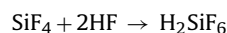
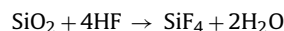
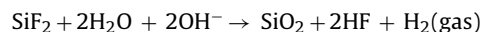
Vacuum sputtered gold films were coated for 25 s on cleaned Si (100) surfaces and annealed in argon atmosphere. The gold metallic thin films form discontinuous and self-assembled globular shape of gold nanoparticles of average diameter 100 nm on the silicon substrate (as shown in Fig. 1b). The annealed silicon substrate was then immersed in aqueous HF solution containing an oxidizing agent AgNO_3 . This will essentially form numerous arrays of nano-sized electroless electrochemical cells. Silver ion deposited on bare portion of silicon surface, served as the cathode, with respect to the silicon surface beneath as anode, whereas, gold nano particles served as anode instead of the silver ions deposited onto it which act as cathode [3]. Silver ions get reduced by gold nanoparticles, while at the interface of silicon surfaces, reduction occurs due to hole injection into it. Then upon reaction of loosely bonded atomic silicon with etchant solution HF, volatile silicate fluoride complexes are formed along with evolution of hydrogen gas [20]. As the reaction progresses, reduced Ag metal particles nucleate on own and dig into the silicon surface [18,20] selectively by forming vertical

aligned silicon one-dimensional arrays of nanowires. The probable complex silver assisted electroless etching reactions are as follows: At cathode site:

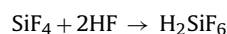
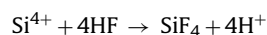


At anode site:

(I) silicon dioxide formation



(II) direct redox reaction



The light weight dihydrogen hexafluoro silicate (H_2SiF_6) complexes are floated onto the solution. The drawn Ag nanoparticles into the silicon wires are washed out thoroughly. Gold nanoparticles, which reside on top of the silicon nanowires are washed away by nitric acid carefully. After thorough washing of silicon substrate, no other impurities were found as confirmed by EDS spectrum in Fig. 1d.

3.2. SEM analysis

The SEM images of electroless metal assisted treated silicon substrate are presented in Fig. 1a; there is a non-uniform and randomly etched silicon surface nanostructure as shown in the figure. As discussed earlier, Ag nano particles reduced quickly by accepting electrons from silicon atom, and are later nucleated by forming irregular shaped structures. The nucleated Ag nanoparticle coagulates and digs into the silicon surface non-directionally, thus forming ill-defined non-vertical silicon nano structures. Now the gold coated silicon substrate is treated for EMD process under the same conditions. As-prepared SiNWs are well aligned in vertical direction of average length and diameter of 3.5–4.0 μm and 75 nm respectively as confirmed from SEM image of Fig. 1c.

3.3. AFM analysis

Fig. 2(a) shows a three dimensional topographical AFM image of SiNWs scanned in a non-contact mode with sample size of 10 $\mu\text{m} \times 10 \mu\text{m}$ at a scan rate of 0.5 Hz. Uniform growth of one dimensional silicon nanostructures with average tip height of 50 nm is observed. From line profiles analyses, as shown in Fig. 2(b), density of SiNWs growth is calculated to be 60 SiNWs μm^{-2} with average spacing of 120 nm.

3.4. Raman spectroscopy

The Raman spectra of the bulk single crystal silicon substrate and SiNWs from the laser power of 35 mW are shown in Fig. 3. The characteristic peak for Si wafer is obtained at 520.61 cm^{-1} , which is attributed to the scattering of the first order optical phonon of c-Si [22]. The first order Raman peak of SiNWs is obtained at 520 cm^{-1} . The intensity of the Raman spectrum for SiNWs increased with

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