Sensing Properties of Assembled Bi_2S_3 Nanowire Arrays

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Keywords: Bismuth Sulphide, nanowire array, conductometric response, relative humidity

Abstract

Bi_2S_3 nanowires were grown in porous aluminium oxide template and a selective chemical etching was applied to transfer the nanowires to a solution. Well aligned nanowire arrays were assembled on pre-patterned silicon substrates employing dielectrophoresis. Electron beam lithography was used to connect aligned individual nanowires to the common macroelectrode. In order to evaluate the conductometric sensing performance of the Bi_2S_3 nanowires, current – voltage characteristics (IVC) were measured at different relative humidity (RH) levels (5 – 80%) / argon medium. The response of the Bi_2S_3 nanowires depending of relative humidity is found to be considerably different from those reported for other types of nanowire RH sensor devices.

Introduction

Semiconducting nanowires have been demonstrated as promising structural elements in conductometric sensors for biological and chemical gas sensing [1, 2]. The excellent sensitivity to environmental adsorbents originates from the increased nanowire surface to volume ratio. Moreover, sensitivity can be tuned by nanowire dimensions, morphology and doping concentration. Recent studies show even ultrasensitive response of nanowires operating in the so called sub-threshold regime, where the charge screening length of the nanowire is lower than its radius and can have a great surface impact to the whole nanowire volume [3].

Relative conductometric humidity sensing is an important field in the sensor industry. Ceramic materials are widely used for this purpose. Other types, including metal oxide nanowire based RH sensors have been also reported [4]. However, humidity sensing mechanism of nanowire sensor devices may become very complex, since the water molecules can have different types of interaction with the nanowire surface, such as chemisorption, physisorption and ionic conduction at higher RH levels. Among the application in the RH sensing devices, it is important to evaluate the RH impact on the nanostructure electrical properties for various analyte sensing at room temperature atmospheric conditions.

It this work we study bismuth sulphide (Bi_2S_3) nanowire sensing behaviour at different RH levels. Bi_2S_3 is an n-type semiconductor where conduction is provided by sulphur vacancies as an intrinsic property [5] causing large variation of the resistivity. Lone pairs of electrons for both bismuth and sulphur atoms can act as active centres for donor – acceptor like interaction resulting in an increased selectivity to the impurities or local sensitivity [6]. Combining these properties with nanometer size geometry, Bi_2S_3 nanowires are expected to be an excellent element in sensor devices. To date, there are only few reports devoted to the Bi_2S_3 nanowire sensor applications. This includes investigations of hydrogen, oxygen sensing and biomolecule detection [7 – 9]. However, detailed research on the relative humidity impact on the Bi_2S_3 electrical properties or application in the RH sensors has not been reported.

To provide high sensing performance and ability to functionalize nanowires for selectivity enhancement, it is advantageous to employ nanowire arrays for sensor device fabrication. Different approaches of nanowire array sensor fabrication have been demonstrated in recent years. These include dielectrophoretically aligned nanowires or lithographically patterned silicon nanowire arrays [10, 11]. In

the proposed solutions, nanowires cannot be accessed individually, or the surface of the fabricated nanowires can present large defect concentration.
In present work nanowires are individually connected and partly suspended, therefore freely accessible surface area is gained, but the high density of the connected individual nanowires can be used to collect sufficient statistical data. The main focus of this study is devoted to the Bi_2S_3 nanowire relative humidity sensing properties at room temperature.

Experimental Section

Synthesis of the Bi_2S_3 nanowires was carried out in a glass tube by decomposition of organometallic precursor placed on the surface of an AAO template as described in details elsewhere [12]. The surface of the Bi_2S_3/AAO nanowire membranes was polished (diamond suspension, 1 – 0.1μm) to remove Bi_2S_3 layer formed on top of the AAO. Nanowire template was dissolved using 9% H_3PO_4 solution [13], nanowires were washed with deionized water and finally transferred to isopropanol using centrifugation.
N-type silicon wafer covered with ~50 nm Al_2O_3 layer grown by the atomic layer deposition (ALD) was used as the substrate. Electron beam lithography (EBL) was applied for electrode patterning. Subsequently dielectrophoresis was used to align nanowires to the selected electrodes (2 MHz; 9 V). To connect individual nanowires and pattern electrodes a second EBL step was performed. Prior metal evaporation, the contact area was cleaned using Ar^+ ion etching (5 keV, 120 μA, 10s).
Electrical characterization was conducted in designed custom built measurement system. Sample was located in a temperature controllable gas chamber with electronic connections and access for gas flow exchange. For conductometric relative humidity response measurements, stable relative humidity level from 5 – 80% was provided by water-glycerol solutions [14]. RH was maintained in the measurement chamber by constant argon flow (2 sccm, Ar, 99.99%) bubbling through the water-glycerol solution with different glycerol concentrations corresponding to the different RH. The actual level of the RH in the measurement chamber was monitored by the hygrometer (HIH – 4010).

Results and Discussion

Figure 1 presents optical images of the nanowire array sensor device. The dielectrophoresis yielded perpendicularly aligned nanowires with respect to the macroelectrode. Aligned nanowires had negligible misalignment angle (≤ 5^o). On average one nanowire with length exceeding 3 μm can be found per 2 μm line along the anchoring macroelectrode edge (Fig. 1, a). Selected individual nanowires with lithographically connected contacts are shown in Figure 1 b, c. Thus, combining dielectrophoresis and electron beam lithography, more than 100 individual nanowires were connected per chip forming a high density individually accessible Bi_2S_3 nanowire array.

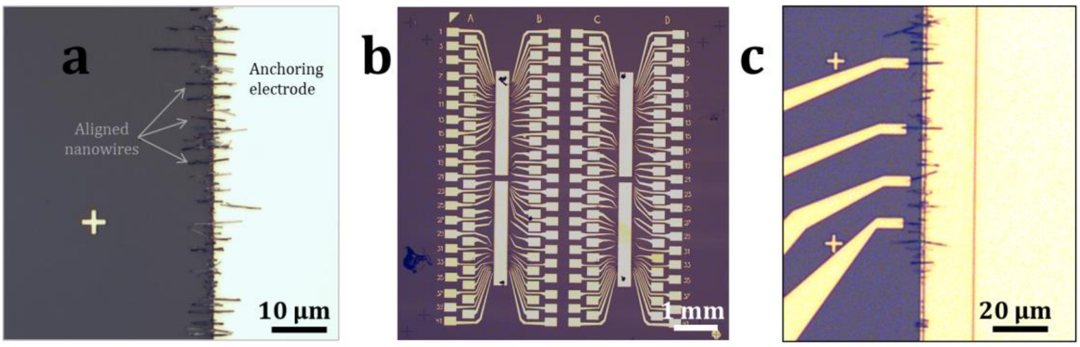

Fig. 1. (a) Dielectrophoretically aligned individual nanowires to the macroelectrode; (b) Overview of the fabricated Bi_2S_3 nanowire array; (c) Electrically connected individually accessible nanowires.

Current – voltage measurements for Bi_3S_3 nanowires demonstrated nonlinear dependencies which can be attributed to the Schottky barrier formation at the metal – semiconductor interface (Fig. 2, a). For the

Bi_2S_3 nanowires it was reported previously as a common characteristics to form a Schottky barrier [15 – 17]. In fact, including argon ion etching step before the metal electrode evaporation during sample fabrication, characteristics with linear dependence were obtained. Thus 90 % of measured curves for all connected nanowires with etched contact area were Ohmic. Some examples of the current-voltage characteristics (IVC) are depicted in the Figure 2, b.

For semiconducting nanowire with metal contacts linear IVC are highly desirable to study the sensing properties. Nanowire with nonlinear IVC provided by Schottky barrier can introduce additional effects, for example, memoresistive mechanism, following by pronounced hysteresis in the IVCs [18]. Relative humidity sensing measurement for Bi_2S_3 nanowires with Schottky barrier affected curves is described elsewhere by our group [19] reporting on humidity induced resistive switching. In this work only Ohmic IVCs for sensing measurements were used at low operational bias voltage (± 40 mV).

Prior RH sensing characterisation, nanowire response to O_2 and SO_2 at inert atmosphere was tested. No measurable changes of the resistance were recorded after nanowire exposure to these analytes at maximum concentration of 1000 ppm respectively. We note that in the earlier reports on Bi_2S_3 nanowire sensors a considerable oxygen sensitivity was present [8]. Sensing response was recorded after exposure to air and observed decrease of resistance was considered mainly due to the oxygen chemisorption, however the RH level in air was not monitored. In present work we observe change of the nanowire resistance by modulating the RH level instead. Thus one can assume to have an increased nanowire selectivity to water molecule sensing for studied nanowires.

To test the nanowire sensing performance, the IVCs at different relative humidity level up to 80% in an otherwise inert medium (argon) were measured (Figure 2, c). The IVCs remained linear in all measured RH levels and change of the resistance was observed if comparing low (6%) and high (80%) RH levels.

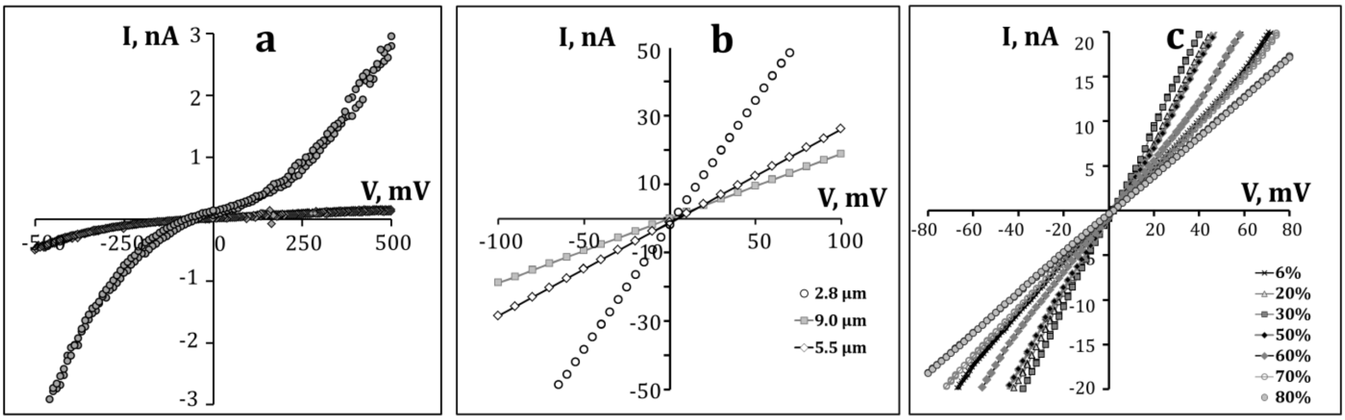

Fig. 2. (a) Non-linear IVCs for individual Bi_2S_3 nanowires; (b) IVCs of the individual Bi_2S_3 nanowires at inert atmosphere and low relative humidity level (RH-5%); (c) IVCs for a Bi_2S_3 nanowire at different RH level / argon environment, L_{nw}= 3.8 µm.

To evaluate nanowire response to the RH, one can plot the nanowire response sensitivity as a function of RH level defining sensitivity as R_{RH}/R_o, where R_o is nanowire resistance at dry argon with RH ~ 5 % (Figure 3, a). Obtained R_{RH}/R_o versus RH dependence had nonlinear behaviour for all measured devices as depicted in the Figure 3. In fact, at the RH level around 40% nanowire response passes through a minimum. Consequently at RH 5 – 40%, nanowire resistance decreased as increasing RH, but overcoming 40%, nanowire resistance apparently start to increase. Therefore, two controversial response behaviours were observed at 5 – 40% and 40 – 80% which can be ascribed to different dominant sensing mechanisms.

Generally presented sensitivity of RH dependencies for n – type semiconducting active elements have linear behaviour in the entire measured RH range with decreasing resistance while increasing the RH [20]. There is also a report for n – type ZnS : Al nanowires possessing maximum in the resistance at RH ~ 50% [21] thus showing reverse type behaviour comparing to Bi_2S_3 nanowire dependence.

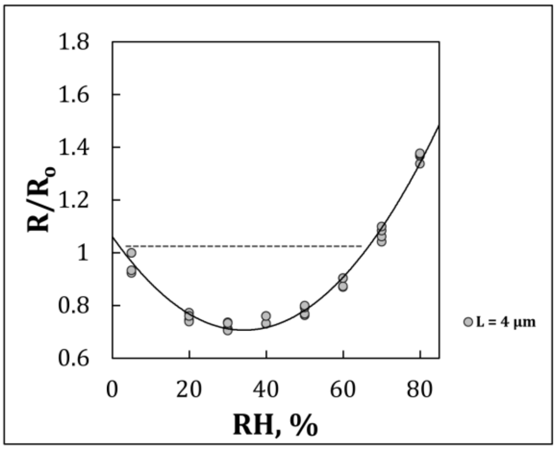

Fig. 3. Relative humidity sensing response of the individual nanowire (bias 40 mV).

Proposed water molecule sensing mechanisms can be treated from material point of view – ceramic, semiconducting or nanomaterial [22]. However, for a reasonable explanation of the resistance modulation with the RH we have to consider semiconducting properties and nanometric size. At the low RH level up to 40%, decrease of the nanowire resistance is consistent with response expected for n – type semiconductor. At room temperature surface physisorbed molecules can release free electrons interacting with surface pre-adsorbed oxygen. This mechanism is often discussed for metal oxide nanowire sensors and is considered as electronic sensing. Assuming thin layer of native oxide Bi_2O_3 on top of the Bi_2S_3 nanowire surface, which can form at increased temperatures [23] during the sample fabrication, one can expect oxygen promoted water molecule physisorption in the low RH levels. Nanowire surface can contain also few static adsorbed molecule layers provided by chemisorption, which produce hydroxyl groups [24]. In general, the formation of the SH- groups can be expected for the sulphide surface after interaction with water molecules. However, this effect has not been observed experimentally as a common trend [25]. Therefore, most likely the surface pre – adsorbed oxygen plays a dominating role in formation of chemisorbed water layer. Further increase of the RH (40 – 80%) causes additional layer adsorption of the water molecules resulting proton hopping through the water layer.

At RH level 65% and higher, measured response has a unique value of the resistance and it increases nearly linearly with RH. At lower RH values, resistance may have similar value at two different RH levels (e.g. 10% and 60%) Hence, some sort of additional range detector would be required for practical sensor application.

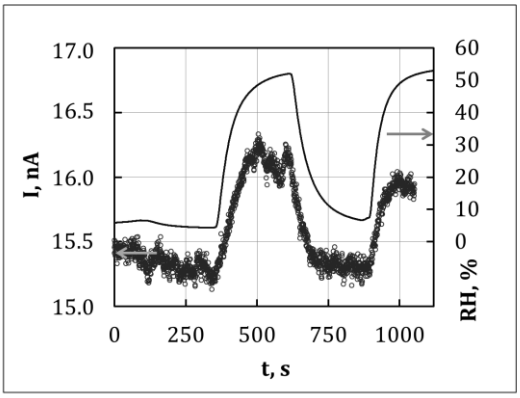

Fig. 4. Dynamic current switching between different RH levels.

Figure 4 represents dynamic response to the RH. It can be seen, that interaction with water molecules is a reversible process. Response and recovery time required to achieve 90% of the equilibrium value is ~50 and 60 seconds respectively.

Conclusions

We have fabricated and characterised individually connected Bi_2S_3 nanowire arrays combining dielectrophoresis and lithography techniques. Employing nanowire contact area cleaning during the sample fabrication, reliable method to produce Ohmic contacts is presented. It was found that individual nanowires exhibit non-monotonous response to the relative humidity indicating on two competing sensing mechanisms at low and high RH levels. Obtained results point out water molecule impact on the Bi_2S_3 nanowire electrical properties.

Acknowledgement

The work was supported by National Program in Materials Science. GK acknowledges the European Social Fund within the project «Support for Doctoral Studies at University of Latvia».

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