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Effect of varying chain length of *n*-alcohols and *n*-alkanes detected with electrostatically-formed nanowire sensor

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ABSTRACT

Recent experimental investigations on the electrostatically-formed nanowire (EFN) sensor have led to promising results for gas phase chemical detection. Herein, we elaborate on the EFN sensor performance by systematically varying the alkyl chain length of target *n*-alcohols and *n*-alkanes. We observe that in addition to the polar target molecules, the sensor is also capable of detecting non-polar alkanes without any explicit additional surface treatment. Moreover, there is a noted increase in the sensor response commensurate with the increasing alkyl chain length for both the alcohols and alkanes tested. The underlying mechanism responsible for the observed phenomena is attributed to an interplay between the alcohol/alkane-silicon oxide interaction, induced surface EFN electric field and inherent molecular properties of our target species.

1. Introduction

As a means to address a myriad of practical challenges, gas phase chemical sensors have emerged as one of the most important, and notably, commercially relevant areas of research. Detection of volatile organic compounds (VOCs) has increasingly become an important focus for gas sensing technologies. The selective sensing of VOCs with high accuracy has led to important developments in the fields of health assessment [1–3], air [4,5] and food [6] quality monitoring and chemical warfare [7,8]. The principle challenge in this field is the integration of the key elements of a potential sensor such as sensitivity, selectivity, dynamic range, robustness, response time, ease of large scale production and miniaturization into a single, practical working device.

Owing to their high surface to volume ratio, nanoscale sensors are very attractive for gas sensing technology [9–14]. Among the most popular (and also commercially available sensors) are the metal oxide sensors (MOS) that measure the change in electrical resistance of the device accompanying an interaction with the target analyte [15–18]. However, MOS sensors typically operate at elevated temperatures which lead to high power consumption and necessitate complicated device assembly. Carbon nanotubes (CNT), on the other hand, are highly sensitive materials and CNT based sensors are well known for their fast response times at ambient temperature [19,20]. In sensor devices, the CNTs must be functionalized in order to detect polar and non-polar analytes with enhanced sensitivity and selectivity [21–24]. Extensive research on the molecular engineering of silicon nanowires (SiNWs) with chemical modifications to significantly enhance their sensing properties has led to a rapid development of this field [7,9,14,25–31]. Molecular modification of SiNWs is crucial for enhancing control over their stability, electrical properties of SiNWs, and their analyte-sensor interaction. Wang et al. have detailed the effect of varying chain length [28] and end groups [32] of the molecular layer attached to SiNWs on their sensor response towards alcohols and alkanes. The dipole interaction between the surface modified layer and the target analytes leads to changes in the initial dipole moment of the molecular layer. The electron donating/withdrawing groups of the layers attached to the SiNW are believed to control the dipole moment orientation of the adsorbed VOCs. This in turn leads to changes in both the threshold voltage and carrier mobilities of the SiNW field effect transistor. Analyzing such changes in several device parameters has led to selective detection

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of the VOCs [29]. The non-polar VOCs, on the other hand, were reported to indirectly influence the effective dipole moment of the organic layer by inducing conformational changes in the monolayer [27,28,33]. Using this technique, several polar and non-polar VOCs were not only selectively detected [29] but also used to sense VOCs linked to cancer from patient breath samples [7,9].

The electrostatically-formed nanowire (EFN) was first introduced in 2013 as a biosensor for real-time detection of femtomolar protein concentrations [34]. The EFN device is an accumulation type three gated field effect transistor with silicon oxide surface that interacts directly with the target molecules. The EFN is referred to the electron conducting channel that is reduced to the nanometer size regime by controlling the surrounding gates. The gate voltages have a strong influence on the size and shape of the EFN formed and can be tuned accordingly. The EFN sensor was shown to detect ethanol in the gas phase with varying sensor response corresponding to different EFN diameters [35]. Moreover, in a recent report, our group demonstrated that the EFN sensor is potentially capable of detecting a single elementary charge [36]. Scanning gate microscopy measurements were used to determine the electrostatic limit of detection independent of the analyte. The major advantages of the EFN over other nanomaterial-based devices are (i) the ability to tune the size and shape of the conducting channel; (ii) EFN is formed sufficiently away from the Si/SiO_2 interface which is typically a dominant source of noise and surface states; (iii) better structural stability; (iv) EFN is more robust and easier to handle with no physical nanometer features in the device. In our previous report, it was shown that the dynamic range of the EFN sensor for any analyte in general (with sensor response > 0) can be significantly enhanced using a single device [37]. The result was demonstrated for ethanol and acetone without any surface modifications or additional/arrays of devices. This is a useful feature unique to the EFN, resulting from its tunable size and shape.

Herein, we elaborate on the EFN sensor response to linear alcohols and alkanes of varying chain length (Table 1). The analytes were exposed to the top SiO_2 molecular gate of the device without any additional surface treatment. It was observed that the sensor not only detected the polar alcohols efficiently, but also responded considerably well to comparatively elevated concentrations of the non-polar alkane molecules. Detection of non-polar molecules with chemically unmodified silicon based devices or SiNWs based sensors has, to our knowledge, not been reported. In general, for a sensor, chemical modifications to the nanomaterial are considered essential to enhance the sensor performance. On the other hand, in the case of the EFN, sensor performance is controlled solely by electrostatic means thus eliminating the need for additional surface chemical modifications. The EFN sensor response was observed to increase in a systematic manner with increase in the alkyl chain length for both the alcohols and alkanes as tested (Table 1). Sensor performance under varying EFN operating conditions was analyzed and possible factors leading to the observations are discussed.

2. Experimental methods

2.1. Materials

All volatile organic compounds tested in this work were of ACS reagent grade purchased from Sigma Aldrich Israel.

2.2. EFN device fabrication

The EFN transistors were fabricated in a semiconductor foundry (TowerJazz, Migdal Haemek, Israel) employing silicon-on-insulator (SOI) technology on Boron doped ($N_A = 1.5 \times 10^{14}$ cm^3) 8-inch SOI wafers (Soitec, France, Berlin) with a bulk resistivity of 750 Ωcm, an SOI thickness of 150 nm and a back SiO_2 layer thickness of 1 μm. Four photolithography masks with a critical dimension of 440 ± 20 nm were used, one to define the trenches, and the other three to implant the dopants for channel ($N_D = 4 \times 10^{17}$ cm^3, Arsenic), source-drain ($N_D = 7 \times 10^{19}$ cm^3, Arsenic), and junction gate regions ($N_A = 2 \times 10^{20}$ cm^3, Boron). The process was simulated using Synopsys TCAD Sentaurus (MountainView, CA, USA) process simulator. Transistors with different surface geometries of the *n*-doped channel were fabricated (length of 5 or 10 μm and width of 500, 750 or 1000 nm) in order to assess the most favorable size for gas sensing. The SiO_2 gate dielectric layer was thermally grown at 900 °C. The wafer was diced to 1 cm^2 squares and Ti/Au contacts were formed by optical lithography and subsequent metal evaporation. The fabrication process was monitored by measuring the doping concentration by SIMS and the distance between the metallurgical junctions by SEM and AFM. The measured parameters served as input to the device process simulations. This way, the EFN device was improved in an iterative process. Devices were wire bonded to chip carriers for electrical characterizations.

2.3. Gas sensing and electrical characterization

Sensing of VOCs was carried out in a controlled nitrogen (99.999% purity) atmosphere in a sealed metallic gas chamber connected to a gas dilution system. The target VOC saturated gas was generated using a bubbler system and diluted with nitrogen at controlled gas flow rates using flowmeters (Key Instruments Series FR2000 Acrylic Flowmeters) to generate different concentrations of the VOC in the chamber. The VOCs introduced in the chamber induce a change in the surface charge density equivalent to that of localized negative charges on the SiO_2 thus forming a molecular gate. This leads to depletion in the electron conducting channel thus reducing the drain current upon the VOC exposure. I_{VOC} was recorded after exposing the device to VOC for 8 min. A photo ionization detector (ppbRAE 3000, RAE Systems) was used as the reference sensor; connected to the sensing chamber in order to monitor the analyte concentration. The electrical characterization of the EFN device (Supplementary information) and the sensing measurements were performed using an Agilent B1500A semiconductor device analyzer.

3. Results and discussion

3.1. EFN sensor characteristics

The electrostatically formed nanowire is referred to the electron accumulated channel formed inside the n-type silicon region (Fig. 1) and controlled by the surrounding gates: (i) two junction gates on either side of the channel, (ii) the back gate and (iii) top 6 nm SiO_2 that serves as the molecular gate and interacts with the target molecules. The voltage applied to the junction gates (both) and the back gate is referred to as V_{JG} and V_{BG} respectively; the drain current and source-drain voltage as I_{DS} and V_{DS} respectively. Fig. 1b shows the $I_{DS} - V_{DS}$ characteristics of the device for different V_{JG}. As V_{JG} becomes more negative, the channel is further depleted, thus increasing the depletion region in the *p-n* region and forming a narrower EFN. As a result, the current (I_{DS}) corresponding to a more negative V_{JG} or a narrower EFN is lesser. Fig. 1c shows the I_{DS}-V_{BG} characteristics for two different V_{JG} before and after exposure to 250 ppm hexanol, demonstrating a typical EFN sensing performance. It is clearly seen that the difference in the I_{DS} before and after exposure, corresponding to the measure of sensor response, increases as both the V_{BG} and V_{JG} become more negative. Increasingly negative V_{BG} and V_{JG} leads to the formation of a smaller and more compact EFN which is observed to be more sensitive. Impact