Development of an autonomous detector for sensing of nerve agents based on functionalized silicon nanowire field-effect transistors

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ABSTRACT

The ability to detect minute traces of chemical warfare agents is mandatory both for military forces and homeland security. Various detectors based on different technologies are available but still suffer from serious drawbacks such as false positives. There is still a need for the development of innovative reliable sensors, in particular for organophosphorus nerve agents like Sarin.

We report herein on the fabrication of a portable, battery-operated, microprocessor-based prototype sensor system relying on silicon nanowire field-effect transistors for the detection of nerve agents. A fast, supersensitive and highly selective detection of organophosphorus molecules is reported. The results show also high selectivity in complex mixtures and on contaminated materials.

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1. Introduction

The high lethality and the ease of manufacturing Sarin-like molecules from inexpensive starting materials render nerve agents a weapon of choice for terrorist attacks [1,2]. Consequently, counterterrorism activities have been strengthened over the past decade to prevent such potential threat. One goal is to develop reliable, sensitive and specific systems for the detection of organophosphorus molecules in urban areas and battlefields. Several technologies are already used and some others are being developed for the sensing of nerve agents: IMS [3], GC/MS [4], enzymatic assays [5], carbon-nanotube based devices [6,7], etc. However the cost, the limited portability, the operational complexity, the false positives and the slow response time make most of these methods inadequate for on-site monitoring devices. As a result, there is still a need for sensitive, compact, low-cost, and low consumption portable devices for nerve agent detection in the field of defence and homeland security.

Silicon nanowire-based field-effect transistors (NW-FETs) are well studied structures [8–12] that give rise to powerful sensors for the detection of chemical species in air [13–16]. For NW sensors operated as FETs, the sensing mechanism is the field-gating effect of charged molecules on the carrier conduction inside the NW [17,18].

We report herein the development and the appraisal of a supersensitive and fast reacting portable hybrid detector of nerve agents based on electrical transduction of a chemical reaction occurring on the surface of a functionalized silicon nanowire field-effect transistor (SiNW-FET). This device bearing the adequate functionality on the SiNW-FET, a power source and a microcontroller for data processing was fabricated to investigate its relevance for the detection of nerve agents in complex environments. The exceptional performances of the SiNW devices enable the detection of nerve agent simulant with high sensitivity and excellent selectivity.

2. Materials and methods

2.1. Sensitive material fabrication

A series of molecular sensors was described elsewhere in which the reaction of a primary alcohol with an organophosphorus compound (OP) initiates an intramolecular cyclization to generate a quaternary ammonium species which can be identified (Scheme 1) [14,19]. In order to investigate the influence of the charge generation on the electrical properties of a SiNW-FET, an anchoring unit may be used to localize the molecular receptor onto the nanowire. For instance, an ethynyl anchoring group was used to perform covalent grafting of the molecular receptor on the Si–H surface by hydrosilylation.

Compound **1** was synthesized in four steps starting from the Kemp's triacid with an overall yield of 40% accordingly to the

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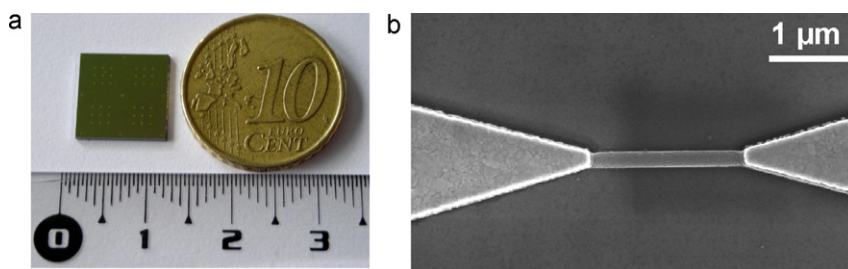
Fig. 1. (a) Image of a chip bearing 36 SiNW-FETs and (b) MEB image of a single SiNW-FET (70 nm thick, 200 nm wide and 2 μm long).

synthetic procedure published elsewhere. FTIR, ^{1}H and ^{13}C NMR, and mass spectrometry spectra were in agreement with literature data [14].

2.2. Field-effect transistor fabrication/portable hybrid detector fabrication/sensor architecture

The SiNW-FETs were fabricated from p-doped (10^{15} B atom/cm^3) silicon on insulator (SOI) wafers (Fig. 1). SiNW-FETs of 70 nm thickness with different lengths and widths (4 μm × 4 μm; 4 μm × 1 μm; 2 μm × 1 μm and 2 μm × 0.2 μm) were obtained by e-beam lithography and dry reactive ion etching steps. The thickness of the SiO$_2$ gate dielectric was 140 nm. Ti/Au (10/100 nm) source and drain contacts were achieved by using e-beam lithography and lift-off process. The Si degenerated substrate was used as back gate electrode.

The semiconducting part of the sensor was functionalized *via* formation of a covalent grafting through thermal hydrosilylation of **1** onto HF-pretreated substrate in refluxing mesitylene for 2 h. We chose to dissociate the electronic part of the device from the sensing element. Thus the transistor chip is connected onto a pluggable plastic card by gold wire bonding for source and drain electrodes and with silver paste deposited onto the back gate electrode (see Fig. 2). Then the sensing card bearing the transistor can be connected to the electronic part of the device through three electrically active pins.

The drain-source and gate-source voltages, respectively V_{DS} and V_{GS}, are applied while the drain-source current is measured as a function of time (Fig. 3).

The prototype can be divided into three main parts: a microcontroller, a functionalized SiNW-FET acting as the transductor, and digital-analog converters with current-to-voltage circuits


Fig. 2. Picture of the device. Insert shows the field effect transistor wire bonded on a card with the three connectors.

interfacing the FET with the microprocessor. The ultra low-power mixed signal microcontroller from Texas Instruments was installed on the printed circuit board equipped with a digital-to-analog converter and a logarithmic amplifier able to measure very low current over a range of six decades. The drain-source current I_{DS} is the signal processed by the microcontroller, and the sensor output is proportional to I_{DS}. The board was equipped with a DC/DC converter (±15 V) that operated from a 9 V battery, and three security alert elements: a LCD text display, a buzzer and a two-color LED.

2.3. Sensor operation/test description

A sampling cycle begins by a calibration step which consists in swipping drain-source current versus gate voltage of the ambipolar transistor, in air, at a constant bias voltage $V_{DS} = -1$ V. Once the transfer curve is acquired, the minimum value of the off-current is identified with the corresponding gate voltage. This particular value of the gate voltage called V_0 is then applied to monitor the drain-source current as a function of time. It has been shown in previous work that upon reaction with OPs the V_0 potential of
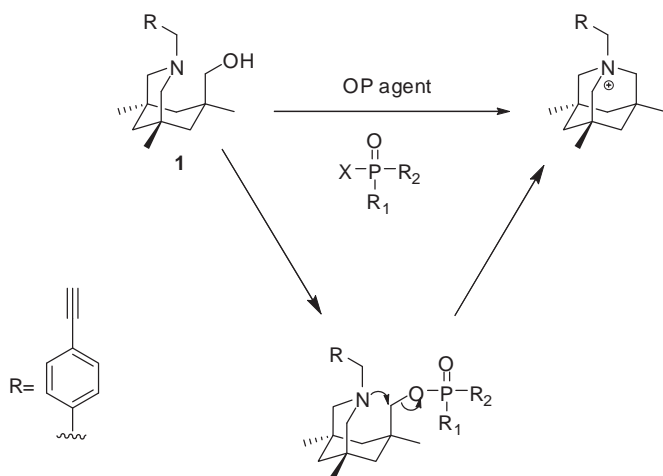
Scheme 1. Reactivity of the molecular receptor **1** towards OPs. R is an anchoring group used to graft the molecule on a specific surface.
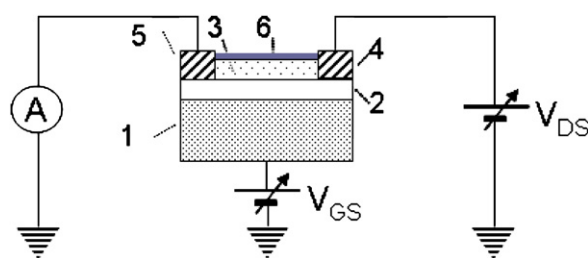
Fig. 3. Scheme of the field-effect transistor based sensor. (1) Highly doped silicon back gate electrode, (2) SiO$_2$ dielectric, (3) Si semiconducting channel, (4) drain electrode, (5) source electrode, (6) monolayer of grafted receptors.
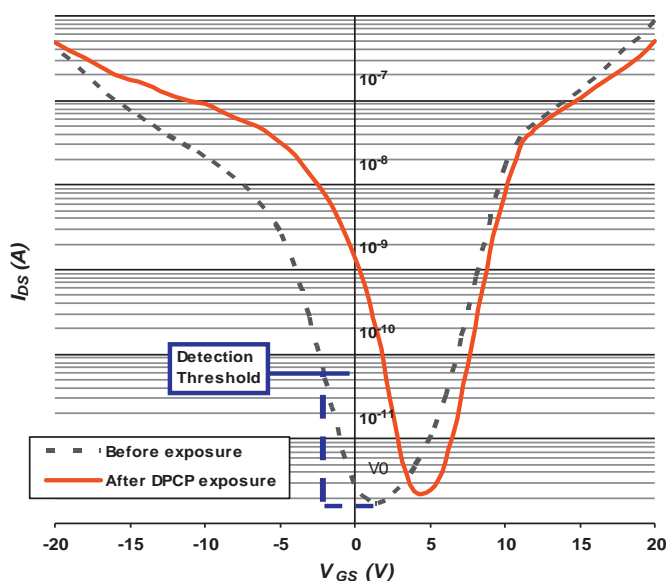
Fig. 4. Functionalized SiNW-FET, I_{DS}–V_{GS} curves at $V_{DS} = -1$ V before (red solid line) and after DPCP exposure (black dotted line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

functionalized FET is clearly shifted to more positive gate voltages with an average variation ΔV_0 of (7.3 ± 3.5) V [14]. As a consequence, the detection threshold is the I_{DS} value measured during the calibration process for $V_{GS} = [V_0 - 3V]$ (i.e. -2.0 V in Fig. 4). The alarm is triggered when the drain-source current reaches the predetermined detection threshold (i.e. $\sim 7 \times 10^{-11}$ at -2.0 V in Fig. 4).

The sensitive area of the FET is then fed by air that may contain analytes. When the air holds organophosphorus compounds like diphenyldichlorophosphate (DPCP), a good simulant of Sarin, then I_{DS} monitored by the device raises. If an increase in drain-source current is detected and if I_{DS} exceeds the previously determined threshold value, then the operator is warned against the possible presence of organophosphorus agents. The alarm status is displayed on the LCD readout along with a blinking LED, and the buzzer set off. A computational algorithm allows the use of a low-power and low-cost microcontroller for data acquisition and analysis. The general testing procedure in the present study was first to acquire an I_{DS}–V_{GS} sweep at a constant bias voltage ($V_{DS} = -1$ V). Then, after stabilization for 30 s in air while monitoring continuously I_{DS} at constant bias voltages ($V_{DS} = -1$ V; $V_{GS} = V_0$), the sensor is exposed to analytes for 10 s. The sensor output, which is proportional to I_{DS} was processed and analyzed using Eq. (1), to give the so-called sensor response. I_{DS}^0 is the drain source current before exposure while $I_{DS}^{10\,s}$ is the drain-source current after a 10 s exposure to analyte vapors.

$$\text{Sensor response} = \frac{\left| I_{DS}^0 - I_{DS}^{10\ s} \right|}{I_{DS}^0} \qquad (1)$$

3. Results and discussion

3.1. Experiments with OP simulants

The transfer characteristics of the functionalized SiNW-FET measured with an Agilent 4155C Semiconductor Analyzer before and after exposure to vapors of DPCP is depicted in Fig. 4. This curve shows a clear shift to more positive gate voltages of the transfer curve when the transistor is exposed to DPCP vapors. When such an experiment is realized with the portable hybrid detector typically in ambient air at 20 °C and 45% relative humidity, a steep increase

Table 1
Values of vapor pressures of tested analytes at 20 °C unless otherwise indicated.

Entry	Compound	Vapor pressure (ppmv)
1	Pentane	550,000
2	Cyclohexane	100,000
3	Toluene	30,000
4	Dichloromethane	460,000
5	Acetone	240,000
6	Diethyl ether	580,000
7	Ethyl acetate	96,000
8	N-methyl pyrrolidone	430 (25 °C)
9	Tetrahydrofuran	190,000
10	Ethanol	58,000
11	Iso-propanol	43,000
12	Pyridine	24,000
13	Propionic acid	4300 (27.6 °C)
14	Water (100% relative humidity)	N/A
15	Hydrogen peroxide 30% in water	N/A
16	Bleach/sodium hypochlorite 5% in water	N/A
17	Dimethylmethylphosphonate (DMMP)	1100 (25 °C)
18	Diesel exhaust gases	N/A
19	Bis-dichlorophenylchlorophosphate	N/A
20	Diphenylchlorophosphate (DPCP)	0.5–0.8

of the output signal (i.e. proportional to drain-source current) is recorded. It should be noted that the sensor works in a cumulative way. Indeed, the reaction between the grafted receptors and the reactive molecules is irreversible, thus V_0 shift can be affected both by the concentration of analyte and time exposure. The increase for a 10 s exposure to vapors of DPCP (500 ppb) gives a sensor response of 78 according to Eq. (1). It has to be noted that when exposed to dry air or air with various relative humidity contents (in the range 0–90%), the signal was found to be very stable. We did not observe neither increase nor decrease of the output signal (Table 1).

We also used a solid simulant named bis-dichlorophenylchlorophosphate which exhibits the same chemical reactivity than OPs and DPCP. To our knowledge, the vapor pressure of this compound has never been reported. However with regard to its known physical properties (melting point 51–56 °C), it seems reasonable to assume that very low content of molecules are present in the gas phase (probably few ppb or even lower, and certainly much less than for DPCP). Nevertheless the sensor gives very satisfactory results and actually detects traces of such material (see Fig. 5).

3.2. Experiments with DMMP

Diphenylchlorophosphate (DPCP) which is the main simulant used in this study, appears as a good mimic for warfare agents like Sarin or Soman since it has both good structural and chemical reactivity analogies with organophosphorus agents. Dimethyl-methylphosphonate (DMMP) is often used as OP simulant. This molecule is clearly a good structural analog to OPs but its chemical
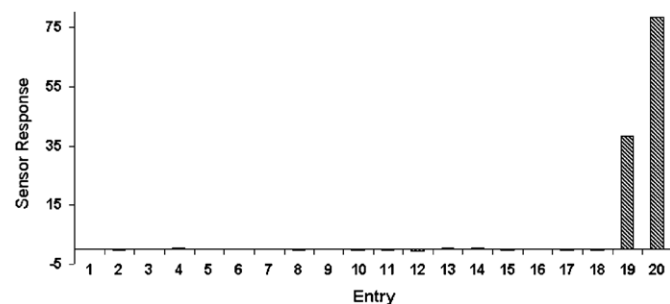
Fig. 5. Sensor response calculated from Eq. (1) for a 10 s exposure at 20 °C to several analytes. The analyte names and their vapor pressures are reported in Table 1.

reactivity does not mimic well the electrophilic behaviour of real nerve agents (methoxy group is a poor nucleofuge). Moreover, due to the fact that this molecule is widely used as a flame retardant, plasticizer, antistatic agent or additive for gasoline, it can compete with the detection of nerve agents in complex environments. In the present study, it is remarkable that the prototype is able to detect very quickly and with an extreme sensitivity DPCP, and does not respond to a structural analog that does not present a similar reactivity to nerve agents like DMMP (Fig. 5).

3.3. Tests with interferents

Fig. 5 shows the sensor response for several analytes that could interfere with the sensor operation. No significant effect was observed when the detector was exposed to high concentrations of organic solvents and other domestic volatile compounds. The selectivity of the sensor was thus excellent even with complex atmospheres such as vapors of perfumes (e.g. Hugo Man® perfume, Faconnable® perfume, Soupline® softener) or diesel exhaust gases (entry 18).

3.4. Demonstration in a relevant environment

We point out that the sensor is able to detect the presence of DPCP in various environments, representative of real conditions. No positive response was observed when the detector was exposed to cotton cloth, paper or soil particles polluted with solvents, but the sensor set off alarm when exposed to DPCP-tainted cloths, DPCP-tainted paper or DPCP-polluted soil (1%, w/w DPCP in sand). The sensor was also exposed for 10 s to various mixtures composed of vapors of organic solvents and at times DPCP. The alarm was triggered only when the Sarin simulant was present.

4. Conclusion

In conclusion, the present study describes the fabrication of a portable, battery-operated, microprocessor-based prototype sensor system based on SiNW-FET for detection of a nerve agent simulants. An extremely rapid, sensitive and highly selective detection of a Sarin-like molecule is reported. Moreover, our results shows that DPCP can be distinguish among other related compounds, in complex mixtures or on contaminated materials. We have now developed more sensitive devices [18] that will be integrated in the same prototype, which should lead to a further increase in performances. To our knowledge, this approach represents the first fully integrated portable device for the detection of Sarin-like molecules based on nanotechnologies.

Acknowledgement

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