

Field Effect Transistor Based on Solely Semiconducting Single-Walled Carbon Nanotubes for the Detection of 2-Chlorophenol

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We report a promoted sensitivity to 2-chlorophenol (2-CP) molecules of a fabricated back gated, interdigitated electrode field effect transistor based on separated semiconducting single-walled carbon nanotubes (CNTFET). The origin of the interaction between the nanotubes that serve as channels across the source and drain contacts and organic volatile compound is suggested due to peculiarities gained after the nanotube separation technique. The semiconducting nanotubes that were used for building-up the CNTFETs had an average diameter of 1.4 nm and have been separated by the efficient aqueous two-phase extraction technique. The advantage of the technique is in the one-step extraction of semiconducting type of conductivity nanotubes with high yield. Chlorophenols are widely studied due to the toxicity and hazardous health effects depending on the exposure. Previously chlorophenols were reported to be not interacting with pristine nanotubes. As prepared CNTFET device demonstrates a detection limit below 100 parts per million for the 2-CP molecules with a reaction time of 150 s. CNTFET devices have good repeatability, low bias stress, and electron charge carrier mobility of $17.5 \pm 0.1 \text{ cm}^2 (\text{Vs})^{-1}$. We discuss possible physical mechanisms of the 2-CP adsorption induced current drop and potential ways to improve sensitivity.

1. Introduction

Single-walled carbon nanotubes (SWCNTs) demonstrate unique electrical, optical, mechanical properties due to their quasi 1D structure.^[1] One-dimensional confinement of electronic states determines the nanotube electronic structure. Deeper understanding of the underlying physics together with the development of processing technologies made SWCNTs become widely used for various applications and devices. SWCNTs are promising for transistor applications.^[2] In order to exclude the shortening of the transistor, obtain high on/off current ratio, and obtain devices with equal properties such as threshold voltage and source-drain tunneling, high purity semiconducting SWCNTs are needed. Depending on their geometry, semiconducting nanotubes possess different band gap value, which also affects the characteristics of the constructed device. Initially SWCNTs were grown within a mixture of semiconducting and metallic

types.^[1] Selective growth achieved by modifying the catalyst's composition and structure can result in production of nanotubes with a high ratio of equal conductivity type, but only with several limited geometries.^[3,4] The post-growth separation techniques allow obtaining various nanotube geometries providing selection of nanotubes with required parameters for exact application,^[5] additional precise electronic structure modification can be performed upon nanotube filling.^[6,7] Aqueous two-phase extraction (ATPE) was recently introduced for SWCNT separation.^[8] It provides very fast processing of nanotubes in large quantities. Moreover, many chemical agents can be used repeatedly making it a cheap method, significantly reducing the overall expenses for the production of semiconducting nanotube based devices. However, separation techniques require different treatments of nanotubes, for example, sonication, centrifugation, introduction of surfactants, etc. These processing procedures may influence the properties of nanotubes that further will be used for production of devices.

CNTFETs (single-walled carbon nanotube field effect transistors) have been applied successfully to the sensitive detection of various gasses such as ammonia (NH₃) and nitrogen dioxide

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(NO₂), hydrogen peroxide (H₂O₂) gas in the parts per million (ppm) range.^[9] Wide variety of volatile organic compounds (VOCs) can be monitored by this type of sensors, including polar and nonpolar molecules.^[10] Moreover selectivity to specifically one type of analyte can be achieved within the background of interfering substances and at different humidity levels.^[10] Sensing applications based on CNTFET rely upon functionalizing the carbon nanotube (CNT) in order to facilitate interaction with the target gas in a way that alters the current-voltage profile of the device. CNTFET sensors advantages are high level of sensitivity, very compact size, wide working temperature ranges, fast recovery times within the seconds, etc. Recently, density functional theory calculations have suggested that Si-doped semiconducting carbon nanotubes may interact with 2-chlorophenol (2-CP) and chlorophenol radicals – precursors in the creation of polychlorinated dibenzo-p-dioxins and dibenzofurans, which are known to be persistent organic pollutants.^[11] Although 2-CP is largely present due to industrial applications, it is highly toxic and widely studied due to potential for carcinogen effects. The lack of cost effective solutions for the detection of chlorophenols motivates the search for new alternatives. We show that nanotubes which undergone the ATPE separation technique also become active to such type of molecules and do not require additional functionalization.

In this work, we demonstrate the fabrication of back gated, interdigitated electrode (IDE) CNTFET based on separated semiconducting nanotubes and evaluate it for potential detection of 2-CP. The conductivity type separation of SWCNTs with an average diameter 1.4 nm was performed by ATPE technique and was aimed on the extraction of pure semiconducting nanotube fraction. We hypothesize that the implementation of processed nanotubes after the ATPE technique provides the additional reactivity and results in promoted 2-CP molecules detection. The gas sensing performance is demonstrated at room temperature with a clear detection limit below 100 parts per million. We study the response on the chemical exposure and define the way to improve the device characteristics.

2. Experimental

2.1. Preparation, Separation, and Characterization of Carbon Nanotubes

SWCNTs were synthesized by the arc-discharge technique. The ratio of semiconducting to metallic nanotubes in the mixture of SWCNTs was estimated as 2:1. In order to suspend nanotubes we use 2 wt.% water solution of sodium cholate (SC). We further tip sonicate the suspension for 4 h in order to achieve a good isolation of nanotubes from each other. To separate SWCNTs from the residual products such as amorphous carbon and catalytic particles, and in order to remove the nanotube bundles we ultracentrifuge the suspension at 150,000 g for 1 h (*Optima Max-E, Beckman-Coulter*, MLA-80 rotor). The extracted supernatant is further used in the study. Separation of the SWCNTs is performed by aqueous two-phase extraction. Suspended nanotubes are introduced to the media with different relative hydrophobicity formed by polyethylene glycol (PEG) and dextran. Variation of PEG and dextran concentrations together

with their relative proportion and surfactant concentration lead to partition of nanotubes with exact semiconducting conductivity type at the top PEG rich phase. More details on the concentration, temperature and other parameters can be found elsewhere.^[12]

2.2. Fabrication of Transistors

CNTFETs were fabricated using photolithography on a p-doped 100 mm silicon (100) wafer with resistivity of 1 Ω · cm. A 160 nm insulating layer of silicon dioxide (SiO₂) was deposited using e-beam evaporator with a residual pressure <10⁻⁶ Torr. Then 2 μm thick AZ NLOF2020 negative tone resist was deposited and selectively exposed to 365 nm UV light using SuSS MJB4 contact aligner. After exposure and post applied bake (1 min, 110 °C) the resist was developed in MIF300 developer for 2 min. A 1-min descum etch was done using Plasmatech O₂ plasma asher (13.56 MHz 50 W). Then, 10 nm chromium (Cr) and 90 nm gold (Au) metal stack source/drain contacts were deposited using e-beam evaporator. A lift-off process in NMP completed the bottom electrode patterning process. Source and drain electrodes of the CNTFET form IDE structure with 25 finger pairs. Each finger is 500 μm long and 10 μm wide. The distance between fingers is two microns. Effective channel width of $W = 27 \mu\text{m}$ was calculated from the areal density of carbon nanotubes ($M = 1.2 \times 10^{14} \text{ m}^{-2}$) and average nanotube diameter of 1.45 nm.

Upon fabrication of IDEs on the Si wafer, CNTFETs were produced by depositing CNTs in aqueous solution of 1 wt.% SC to the sample surface *via* a micropipetter. The reported results are well reproducible and have been obtained on multiple fabricated devices.

2.3. Characterization of Transistors

Characterization of CNTFET was performed using an HP 4145 A Semiconductor Parameter Analyzer (SPA) in conjunction with a probe station and a Lab View user interface. Electrical characterization was performed in the N₂-filled glovebox with <0.1 ppm of oxygen and water. A gate sweep technique was used to determine the mobilities of CNTs under both N₂ atmosphere and under 2-CP vapor exposure (vapor pressure 0.308 kPa). The voltage between source and drain was fixed at 10 V, while the gate voltage was varied from 0 to 10 V.

3. Results

The choice of SWCNTs for the CNTFET fabrication is important as nanotube electronic properties are governed by their structure. The band gap value inversely depends on the diameter. CNTFETs that are utilizing narrow diameter nanotubes below 1 nm demonstrate the lowest on-current due to the higher Schottky barrier height (SBH) value at the contact metal-nanotube junction.^[13] Moreover the existence of the nanotube diameter distribution has a greater influence on the variation of the SBH value for the small diameter tubes and therefore the difference between characteristics of the

fabricated devices becomes more pronounced.^[14] Application of SWCNTs with large diameters significantly influences the off state current, roughly rendering the optimal nanotube diameters between 1.2 and 1.7 nm.^[15] For the CNTFET fabrication we used arc-discharge SWCNTs with an average diameter of 1.4 nm. The suspension of nanotubes was prepared in 2 wt.% water solution of sodium cholate (SC) with further tip sonication. The separation was performed by the ATPE technique.^[12] The method is based on the interaction of suspended surfactant covered nanotubes with two phases of media with different relative hydrophobicity. Depending on the conductivity type SWCNTs get covered differently with surfactant, which leads to the selection on the hydrophobic interface between nanotubes and the media. SWCNTs migrate between one of the phases depending on the conductivity type. In our case during the separation procedure semiconducting nanotubes covered with greater extent by SC predominantly move to the top phase, leaving the metallic ones at the bottom. According to the optical absorption spectra (**Figure 1**) the relative amount of semiconducting nanotubes after the separation can be estimated as 98%. The approach for the relative amount estimation is presented in Ref. ^[5], while the fitting procedures of the nanotube absorption spectra are discussed in detail in Ref. ^[16].

CNTFETs were fabricated using photolithography on a p-doped 100 mm silicon (100) wafer with resistivity of $1 \Omega \cdot \text{cm}$. An IDE design was selected to maximize the probability that a randomly distributed CNT will make contact with both source and drain electrodes. IDEs were designed with $2 \mu\text{m}$ spacing. SWCNT dispersion was drop-casted and dried at 150°C on the top of gold IDE structures on Si/SiO₂ substrate to complete CNTFET structures. The substrates were then dried in air for 1 h. Thermal annealing (1 h at 161°C and 30 s at 400°C) on a hot plate was utilized to sublime the excess of residual SC that was present on the tubes due to the separation process. **Figure 2** shows the scanning electron microscopy images of the IDE structures before and after the annealing steps. It can be seen that thermal annealing is effective in removing most of the SC, leaving carbon

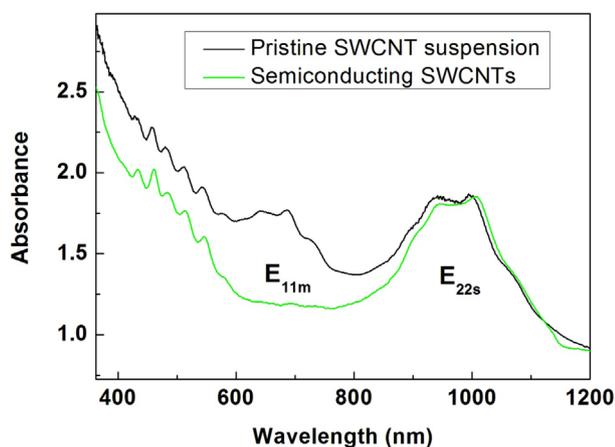


Figure 1. Optical absorption spectra of arc-discharge SWCNTs before and after the separation procedure.

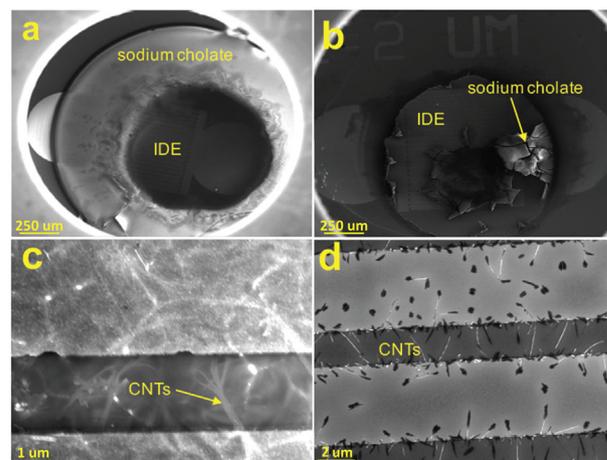


Figure 2. (a) SEM image of sodium cholate on CNTFET before annealing process. (b) SEM image of CNTFET after annealing. (c) and (d) show higher magnification of IDE spacing after annealing using SEM. The visible strands are CNTs.

nanotubes randomly distributed between source and drain electrodes (**Figure 2(c)**). The average number of SWCNTs on a device was estimated from SEM image to be $N_{\text{CNT}} \approx 120 \mu\text{m}^{-2}$. The amount of deposited nanotubes between the electrodes defines the density of the nanotube network leading to the differences in the gas sensing mechanism.^[17] For dense nanotube networks the major contribution for the sensitivity is due to the nanotube junctions, understating the influence form nanotube-electrode contacts and direct gas adsorption on the nanotubes. In our CNTFETs the amount of nanotubes junctions is less than the nanotube crossing between the electrodes making the latter mechanisms of gas sensing becoming substantial.

Results from electrical characterization of CNTFET under exposure to 2-CP are presented in **Figure 3**. Device was tested in pure N₂ atmosphere to avoid possible additional effects oxygen and water can have on CNTFET transport properties.^[18] The square root of source-drain current versus gate voltage can be used to calculate the saturation mobility (μ), using approximate equation for a MOSFET:

$$I_{\text{SD}} = \frac{\mu C_i W}{2 L} (V_g - V_{\text{th}})^2 \quad (1)$$

where V_g is the gate-source voltage, V_{th} is the threshold voltage, W , L , and C_i are the channel width, length and capacitance, respectively.^[19] A set of seven consecutive measurements was taken to ensure stable operation of the device and low hysteresis. Electron saturation mobility of $17.5 \pm 0.1 \text{ cm}^2 (\text{Vs})^{-1}$ was calculated using Eq. (1). A stark drop of the source-drain current and as well as the decrease of slope of the square root of current versus gate voltage can be observed when CNTFETs are exposed to 2-CP (**Figure 3(a)**). At $V_g = V_{\text{SD}} = 10 \text{ V}$, drain current dropped ca. 25 times. In the same time, a significant statistical variation of the I_{SD} was also observed. As we argue below, at this point formula (1) may not be applicable to calculate the saturation mobility anymore.

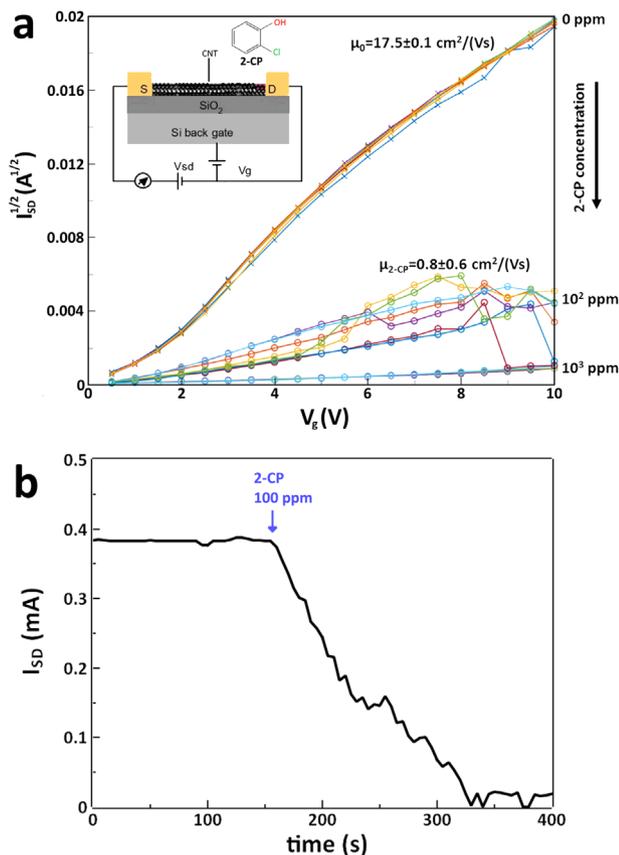


Figure 3. CNTFET device response in N_2 and after the 2-chlorophenol (2-CP) exposure at ambient conditions. (a) Transfer characteristic change as a function of 2-CP concentration. Every measurement was repeated 7-times to ensure that bias stress is minimal and effect of the solvent is persistent. Gate sweep rate 4 V s^{-1} , bias voltage $V_{SD} = 10\text{ V}$, SiO_2 (dielectric layer) thickness = 160 nm . Insets: Scheme of the CNTFET device and sketch of the 2-CP molecule chemical structure. (b) Source–drain current decay versus time after exposure to 100 ppm of 2-CP.

Yet, from engineering standpoint, as the I_{SD} versus V_g for $V_g \gg V_{th}$ is still a linear curve, Eq. (1) shows effective mobility drop to $0.8 \pm 0.6\text{ cm}^2\text{ (Vs)}^{-1}$ after being exposed to 100 parts per million (ppm) of 2-CP and beyond measurement accuracy for 1000 ppm . The characteristic time response of the nanotube 2-CP detector is around 150 s (Figure 3(b)). Sensor recovery can be achieved by external heating. According to the data provided by Agency for Toxic Substances and Disease Registry^[20] the obtained CNTFET detection limit is well below the limit that causes the disease.

Moreover, based on the noise level we estimate a potential sensitivity of the fabricated structures to be 10 ppm . The detection limit was estimated from signal to noise ratio using Rose criterion, taking into account that the root mean square of the noise after exposure to 100 ppm of 2-CP was 0.007 mA . However, presence of other gases in atmosphere can significantly affect this value due to the additional effects described above. Further improvement of the sensitivity was predicted for nanotubes doped with silicon.^[11]

4. Discussion

We believe there could be three possible physical mechanisms responsible for the CNTFET current drop under 2-CP exposure. Since we have not observed a systematic shift of the V_{th} , we conclude that unlike other gases 2-CP does not directly dope CNTs.^[21] However, the I_{SD} may still be dropped because of (i) decreased current injection; (ii) decreased mobility; (iii) decreased gating capacitance, or a combination of these three contributions. Indeed, Heinze et al. have shown that CNTFETs can operate as an unconventional Schottky-Barrier (SB) transistors and that adsorbed gas can raise the metal electrode work function, which would hinder the n-type transport.^[22] Unlike the doping case SB does not cause a significant shift of the V_{th} , yet the current drop in the channel can be several orders of magnitude. This mechanism is often assumed in case of physisorption of gases with no direct CNT charge transfer.^[22] Adsorption of 2-CP may cause a drop of charge carrier mobility in the FET channel due to additional scattering centers/traps introduced in the CNT channel.^[23] Finally, the capacitance of the channel can be affected, which can significantly decrease gating efficiency.^[24] If only the second presented mechanism would take place, it would still be possible to use Eq. (1) for mobility calculation. Yet, high statistical error due to signal noise makes the applicability of it quite limited. In either of three cases, the detection limit of our CNTFET sensor is determined by the amount of adsorbed 2-CP. In our processing method we use SWCNTs that undergone the separation procedure.^[12] It comprises the sonication treatment for the debundling of pristine nanotubes and effective coating with surfactant of each nanotube or small bundles. Sonication is known to introduce defects and shorten the total length of the nanotubes. Despite the fact that we use small intensity sonication and short processing times the appearance of defects can be detected by the slight intensity increase of the D (disorder-induced) mode in the Raman spectra. An increase in the number of defects in nanotube walls promotes the reactivity/adsorption of 2-CP molecules. In general several mechanisms depending on the environment can be responsible for the interaction between chlorophenols and carbon nanotubes.^[25] Among them are interplay between π - π bands that can be additionally promoted by charge transfer and hydrophobic interaction. Before the gas exposure the CNTFET was annealed and the excess of the surfactant was removed. We point that the long duration and high temperature annealing should be excluded as it may lead to the p-type doping of the SWCNTs due to the formation of carbon-oxygen bonds, while 2-CP is known to be an electron acceptor. Additionally, semiconducting nanotubes are less oxidized compared to metallic ones due to the electronic structure, specifically presence of band gaps for semiconducting tubes. Introduction of defects increases the electrostatic interaction between the nanotubes and gas molecules. During the separation by ATPE the nanotubes migrate to the regions depending on hydrophobicity. The semiconducting nanotubes that move to the polyethylene glycol-rich phase demonstrate more pronounced hydrophobic properties compared to other tubes that were present in the pristine non-separated suspension.^[8,12] We assume that the chemical reactivity of separated semiconducting nanotubes with 2-CP gas can be explained by

the promoted π - π interaction and partially accompanied by the influence of the nonpolar interface between the nanotubes and molecules.

In this work, we only show the capability of CNTFET to detect 2-CP molecules with high sensitivity. Practical application of this approach in medical and environmental fields will, however, depend on selective detection of 2-CP in the mixture of different analytes and particularly the confounding ones. As it has been recently shown, it is generally possible to discriminate between similar compounds using single FET device and various pattern recognition techniques.^[26] Along with that diminishing the response to water is a major step towards e.g. the development of sensors for breath testing. While experimental evaluation of humidity effects are beyond the scope of this work, we expect that CNTFET exposure to water vapor may significantly complicate 2-CP detection due to the bias stress effects such as shift of V_{th} and hysteresis. These effects however might be partly mitigated using pulsed characterization.^[27]

5. Conclusions

In summary, we demonstrate that CNTFET based on the separated semiconducting SWCNTs provides the sensing of the 2-CP with the potential response level of 10 ppm. Nanotubes were processed by a post growth ATPE separation technique that resulted in the 98% enrichment of semiconducting SWCNTs with an average diameter of 1.4 nm. CNTFETs were fabricated by drop-casting of SWCNT suspension on gold IDE structure with followed annealing step to remove sodium cholate surfactant molecules. As prepared devices show stable operation with low bias stress and electron transport with carrier saturation mobility of $17.5 \pm 0.1 \text{ cm}^2 (\text{Vs})^{-1}$. Device exposure to 100 ppm of 2-CP results in stark drop of the drain current in ca. 150 s and increased noise level. We attribute high sensing level to the peculiarities of the separated nanotubes leading to increase of electrostatic interaction. The chemical reactivity is associated with promoted π - π interaction together with the nonpolar interface between 2-CP molecules and semiconducting SWCNTs. The demonstrated CNTFET device is a cost effective solution with fast response time to detect even low levels of 2-CP molecules that are widely spread in the environment, but with that toxic to the aquatic life and demonstrate potential to cause carcinogen effects.

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Conflict of Interest

The authors declare no conflict of interests.

Keywords

2-chlorophenol, field effect transistors, phase separation, single-walled carbon nanotubes

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