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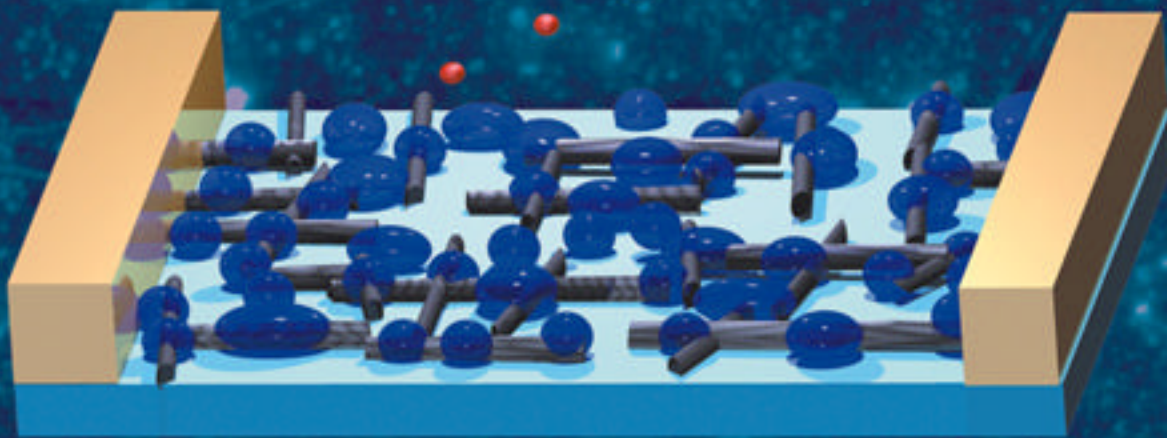
ADVANCED MATERIALS

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of the filter were measured using condensation particle counters (TSI Inc. model 3022A). Submicrometer particles entering the counters are grown into micrometer sized droplets by condensation of a supersaturated vapor of 1-butanol onto the particles, then counted by laser light scattering. The particle concentrations were averaged over ten measurements at each particle size. Filter experiments were repeated at least twice to ensure reproducibility. The pressure drop after filtration was also measured using previously described methods.

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Nanoelectronic Carbon Dioxide Sensors**

By Alexander Star,* Tzong-Ru Han, Vikram Joshi, Jean-Christophe P. Gabriel, and George Grüner

Nearly all biologically significant reactions result in the production, or removal of carbon dioxide. Therefore, the sensing

of CO₂ is important in a broad variety of applications. CO₂ sensors are currently used to monitor indoor air quality, and in capnography—the measurement of CO₂ in respiration during medical procedures. For these applications, the current technology—infrared spectroscopy, is limited by its power consumption, and size. Although a number of simplified CO₂ sensors have been proposed,^[1] many significant problems, such as direct detection, low power consumption, and room temperature operation still remain unsolved.

Field-effect transistors fabricated using carbon nanotubes (NTFETs)^[2] have been recently explored as chemical^[3,4] and biological^[5] sensors. The response of the device characteristics to chemical analytes occurs via charge transfer between the NTFET and the analytes, as evidenced by experiments involving electron-donating (NH₃) and electron-withdrawing (NO₂) molecules.^[2],3a] Recent studies also demonstrate the effect of electron negativity of aromatic compounds on the NTFET electronic characteristics.^[4] Whereas the NTFET devices are sensitive to the presence of strong charge donors and acceptors, they are not sensitive to weak Lewis acids or bases such as H₂, CO₂, and CH₄. Specific sensitivity can be achieved by employing recognition layers that induce chemical reactions that modify the NTFET device characteristics. A catalytic-reaction-based sensing of H₂ has been reported,^[3c] together with a demonstration of a charge-transfer reaction-based sensing mechanism. Both mechanisms work at ambient temperature.

In this communication, we report the design and fabrication of chemically functionalized NTFET devices for CO₂ sensing.^[6] Figure 1a displays the sensor architecture: a NTFET transducer functionalized with a recognition layer specific for CO₂ gas. Although the chemical functionalization of carbon

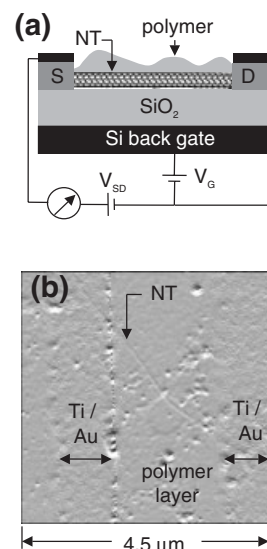


Figure 1. a) Schematic representation of a field-effect transistor (FET) device with a carbon nanotube contacted by two Ti/Au electrodes (source and drain) and a silicon back gate. Carbon nanotube conducting channel is exposed to and covered by a polymer layer. b) Atomic force microscopy (AFM) (tapping mode) image of the actual nanotube device coated with polymer layer.

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nanotubes for sensor applications has been recently explored,^[7] covalent modification has the disadvantage that it disrupts the physical properties of carbon nanotubes thus leading to a loss of conductance. Therefore, we have employed a supramolecular approach, namely, the noncovalent functionalization of carbon nanotubes, by employing polymer coatings.^[8,9] Generally, organic recognition coatings provide synthetic versatility and they can be chemically modified for high CO₂ sensitivity. Moreover, polymers are easily processable for different coating procedures, including spin-coating, dip-coating, drop-casting, and microspotting. The microspotting technique is important for the fabrication of multiple sensors in a sensor array.^[3d,3f] An additional advantage for fabrication lies in the fact that polymer coatings modify^[10] the characteristics of nanotube FET devices and thus the coating process can be readily monitored.

For the CO₂ selective recognition layer, we have used a mixture of poly(ethyleneimine) (PEI) and starch polymers. The proposed mechanism of CO₂ sensing using PEI/starch-coated NTFETs involves the adsorption of CO₂ gas in the polymer coating, followed by the establishment of an equilibrium involving water and PEI amino groups. PEI, a highly branched polymer with 25 % primary, 50 % secondary, and 25 % tertiary amino groups, can effectively adsorb CO₂ from the gas mixture.^[11] CO₂ is generally an unreactive molecule, but it does combine with primary and secondary amines at ordinary temperatures and pressures to form carbamates.^[12] The chemistry between CO₂ and amines is essentially an acid–base equilibrium (Fig. 2a). The chemical reactions lower the total pH of the polymer layer and alter the charge transfer to the semiconducting nanotube channel, resulting in the change of NTFET electronic characteristics. However, we have found that this sensing mechanism does not work well in the case of polymer layers consisting only of the PEI polymer. A combination of PEI and starch polymers in the CO₂ recognition layer is needed. Starch, a mixture of linear component amylose and branched component amylopectin,^[13] interacts strongly with nanotubes^[9] and affects CO₂ reaction with PEI amino groups. We suggest that the presence of the starch attracts more water to the NTFET surface due to the hygroscopic nature of the polymer. When the reactions occur in the presence of hygroscopic starch, the interaction of carbon dioxide with H₂O shifts the equilibrium due to the competing formation of car-

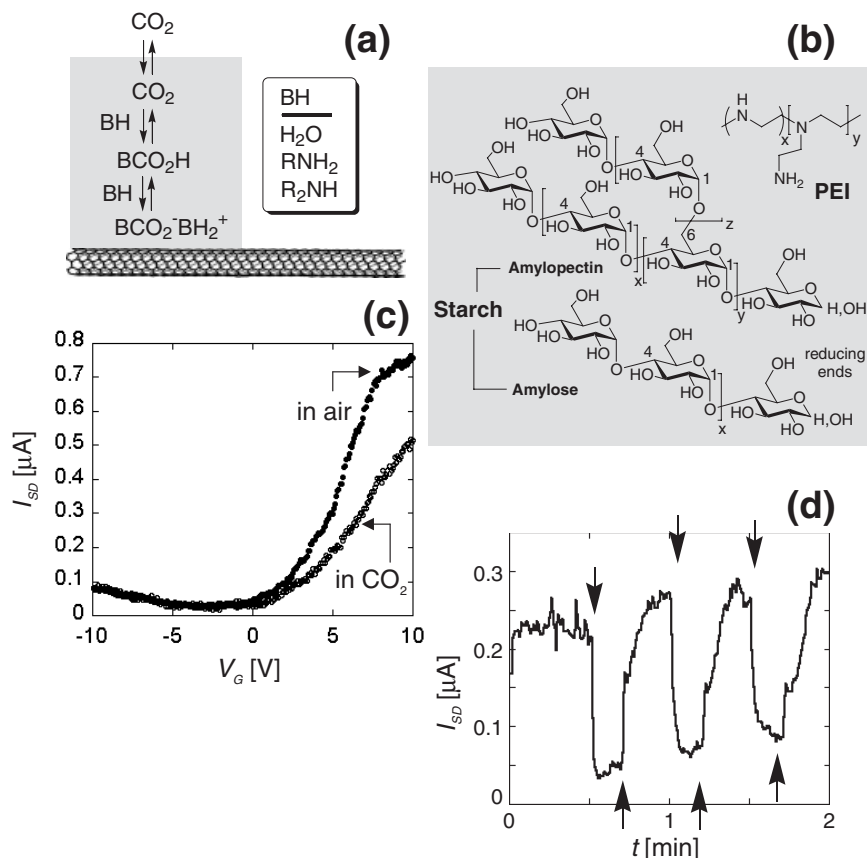


Figure 2. a) Mechanism of CO₂ chemical sensing using polymer-coated carbon nanotubes. The polymer layer possesses amino functionalities, which in the presence of CO₂ undergo a reaction to carbamates, resulting in a change of carbon nanotube FET doping. b) Chemical structures of poly(ethyleneimine) (PEI) and starch, a mixture of amylose (the linear component) and amylopectin (the branched component). c) The source–drain current (I_{SD}) versus gate voltage (V_G) of the PEI/starch-coated carbon nanotube FET device ($V_{SD} = 1$ V) in air and in 100 % CO₂ gas. d) Current (I_{SD}) versus time (t) response to 100 % CO₂ gas of the device in air at ambient conditions (V_G (effective) = +5 V, $V_{SD} = 0.8$ V). Arrows indicate when air was switched to CO₂ gas.

bonate and bicarbonate ions (Fig. 2a). This subsequent increase in the local CO₂ concentration in the polymer recognition layer, likely results in greater protonation of PEI amino groups.

The NTFET devices discussed in this study contain semiconducting SWNTs as the source, S, to drain, D, channel. The dependence of the source–drain current, I_{SD} , as a function of the gate voltage, V_G , was measured from +10 V to –10 V gate voltages. We refer to this response as the I – V_G curve and this curve is used in order to characterize the device electronics. Coating the NTFET device with a mixture of PEI and starch polymers results in an n-type NTFET device characteristic (Fig. 2c). This effect is attributed to the electron-donating property of the NH₂ groups in the PEI polymer.^[10a] CO₂ reaction with the PEI/starch polymer coating results in carbamate formation, which reduces the overall electron-donating effect of PEI, and leads to a device characteristic that is consistent with removal of electrons from the device. Since the device characteristic is modified only for positive gate voltages (see

Fig. 2c), leaving the transconductance in the negative gate voltage region unaffected, we also suggest that upon carbamate formation, geometric deformations in the polymer layer may occur leading to scattering sites on the nanotube, and thus a reduced conductance. This mechanism was proposed earlier for protein sensing using polymer coated NTFETs.^[5a] The observation of reduced conductance at positive gate voltages with no measurable change in the threshold voltages (Fig. 2c) strongly supports the second mechanism, i.e., polymer layer deformation upon CO₂ binding with consequent changes in the NTFET electron doping.

The change in the device characteristic upon CO₂ exposure can be used for sensor design. Source–drain current (I_{SD}) at positive effective gate voltage ($V_G(\text{effective}) = +5$ V), where the greatest change occurs in the $I-V_G$ curve, is recorded during three short exposures to CO₂ gas in air at room temperature (Fig. 2d). The response and recovery times are of the order of a few seconds. However, the response and recovery times become slower for each consequent gas exposure, indicating CO₂ saturation at the polymer/carbon nanotube interface. The magnitude of the CO₂ response at constant gate voltage conditions is larger than that measured from $I-V_G$ curves. The CO₂ response is approximately 75 % of the change in the device conductance, whereas the $I-V_G$ measurements show only a 25 % change between the response in air and in CO₂ (Fig. 2c). We believe that the sweeping of the gate voltage in $I-V_G$ measurements can interfere with the BCO₂⁻BH⁺ charges that are formed upon CO₂ binding in the polymer layer and, therefore, shift the equilibria (Fig. 2a) towards the original polymer NTFET characteristics. This phenomena is somewhat related to the recently published concept of erasing charges in photoactive polymer/carbon nanotube interfaces by sweeping the gate voltage.^[14]

In order to improve the required sensor characteristics, the polymer layer was optimized for sensor performance by changing the ratio of polymers, deposition conditions, and resulting polymer layer thickness. Modifications in the sensor platform were also made to optimize the transducer electronic characteristics and its subsequent response to CO₂ gas. For example, the use of nanotube networks^[2k] between the electrodes not only retains the FET behavior but also results in more reproducible electronic characteristics before and after recognition layer deposition. Figure 3 shows the response to CO₂ gas for an optimized PEI/starch-coated nanotube network FET (NTNFET) sensor. The response to CO₂ gas is fast and reproducible at low concentrations, and has a wide dynamic range for CO₂ concentrations from 500 ppm to 10 % in air.

The environmental effects (temperature, relative humidity, O₂ concentration, etc.) on the CO₂ sensor performance as well as cross-sensitivity with other gases are currently under investigation. These sensors are expected to be cross-sensitive to strong acidic gases, such as NO_x and SO_x. For example, NTFET sensors with PEI coatings are known for detecting NO₂ at less than 1 ppb concentrations.^[3d] Therefore, in CO₂ sensor applications where cross-sensitivity with NO_x/SO_x

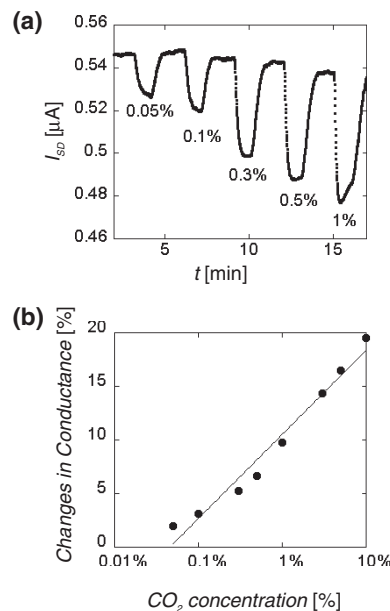


Figure 3. Response of the carbon nanotube sensor to CO₂ gas. a) $I_{SD}(t)$ of the carbon nanotube FET device recorded under bias voltage (V_{SD}) of 0.2 V and gate voltage (V_G) of +6 V in a flow cell (air, RT, RH = 80 %). b) Calibration curve of the sensor at 0–10 % CO₂ concentrations.

gases is an issue, sensor filters and/or encapsulations may be required in order to neutralize the effect of these gases.

In conclusion, we have developed a nanoelectronic sensor, that allows the electronic detection and measurement of CO₂ gas at ambient temperature. The sensor, based on polymer-coated NTFET architecture, shows promising sensor characteristics, such as high sensitivity and precision at low CO₂ concentrations. The NTFET also offers potential for a mass produced sensor that uses nanometer-scale, millisecond-responding films of polymers. Its small size and low power consumption mean that it has enormous potential in wireless sensing for industrial and medical CO₂ sensor units.

Experimental

NTFET and NTFET devices were prepared according to published procedures [2k], using standard photolithography techniques on 100 mm wafers. NTFET devices were fabricated using SWNTs grown via chemical vapor deposition (CVD) at 900 °C using dispersed iron nanoparticles as growth promoter and a methane/hydrogen gas mixture. Electrical leads were patterned on top of the nanotubes from titanium films 30 nm thick capped with a gold layer 120 nm thick. After conducting initial electrical measurements in order to establish the device characteristics, the substrates were submerged in a 10 wt.-% solution of poly(ethyleneimine), PEI (average molecular weight ~25 000, Aldrich chemicals) and starch (average molecular weight 10 000, Aldrich chemicals) in water overnight, followed by thorough rinsing with water. A thin layer (<10 nm) of polymer material coated the devices, as observed by atomic force microscopy (Fig. 1b).

Electronic measurements of NTFET devices, such as current flow between S/D electrodes as a function of applied gate voltage, were conducted using a semiconductor parameter analyzer (Keithley 4200).

For CO₂ sensing studies, chips with multiple NTFET devices were wire bonded and packaged in a 40-pin CERDIP package before functionalization with PEI/starch polymers. The polymer functionalized packaged devices were assembled in a flow cell in which air or CO₂ gas mixtures could be introduced to the devices. The low concentrations of CO₂ were achieved by mixing different proportions of air and 10% CO₂ in air with a CSSI 1010 precision gas diluter (Custom Sensor Solutions, Inc., Naperville, IL).

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Template-Assisted Fabrication of Dense, Aligned Arrays of Titania Nanotubes with Well-Controlled Dimensions on Substrates**

By Melissa S. Sander,* Matthew J. Côté,* Wei Gu, Brian M. Kile, and Carl P. Tripp

Nanotubes hold great potential for various applications due to their high surface-to-volume ratio, the ability to control their properties by tuning their dimensions, and, in contrast to zero-dimensional nanoparticles, a geometry that facilitates

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