Highly sensitive, transparent, and flexible gas sensors based on gold nanoparticle decorated carbon nanotubes


1. Introduction

There exists an increasing worldwide demand for sensors, in particular for standalone and mobile systems, which call for small, low power and flexible devices. Generally nitrous oxide (NO₂) and ammonia (NH₃) are model compounds for gas sensing due to their oxidising and reducing properties. Metal-oxide–semiconductor (MOS) and solid electrolyte (SE) sensors with typical detection limits of 1–1000 ppm at an operating temperature of a few hundred degrees Celsius are commercially available [1–5]. Although these types of sensors are inexpensive and robust, they do suffer from high energy consumption and cannot be fabricated on flexible substrates.

In recent years, nanowires [6–10] and single-walled carbon nanotubes (SWCNTs) [11–13] have been shown to act as ultrasensitive chemical and biological sensors because of their large surface-to-volume ratio with unique physical and electrical properties. Chemical field-effect transistors (ChemFETs) or chemically modified resistors (chemiresistors), in which nanotubes or nanowires act as the conduction channel between two electrodes, work at room temperature and, therefore, have low power consumption. The conductivity of the channel is changed by chemical doping, which can be measured electrically. For SWCNTs, the π-electron system is fully exposed [14] and, therefore, their electrical properties are extremely sensitive to charge transfer and chemical doping from adsorbing species. So far gas and aqueous solution sensors with detection levels of the order of ppm or sub-ppm have been reported [15]. This matches commercial metal oxide film sensors at room-temperature, avoiding the energy intensive operation at elevated temperatures. Furthermore, SWCNT films can be produced cost effectively by spraying into transparent and flexible films, qualifying them for an extended range of applications.

However, SWCNTs are generally grown as mixtures of semiconducting and metallic nanotubes. This can be critical for sensitivity, reproducibility, and reliability. When using large networks of SWCNTs, this problem averages out to a certain extent. However, for thicker films the detection limit rises as the inner tubes are blocked from interacting with target molecules as they cannot penetrate into the network [11]. Thus, it is important to be able to create thin, but well conducting networks and avoid aggregation of the SWCNTs into bundles during deposition [16]. Despite the low sensitivity of network film structure sensors, their simplicity and low production cost make these devices suitable for fabrication processes. Recently, various functionalisation types such as metal particle [17,18] and...
2. Materials and methods

Commercial SWCNTs (IJin Nanotech) were used to make network films. The as-received SWCNTs were dispersed in water using surfactant-assisted ultrasonication, followed by centrifugation to remove agglomerates and, finally, spray-coated onto PET substrates as described in previous work [16]. The as-prepared SWCNT films were decorated by electron-beam evaporation (CHA Mark 50) targeted at 1 nm Au at a pressure of $-3 \times 10^{-6}$ Torr. As a result, AuNPs with typically lateral size lower than 10 nm uniformly covered the surfaces around each individual SWCNT (Fig. 1(a)).

Electrical contact electrodes of 40 nm Au atop an adhesive layer of 20 nm Ni were deposited by sputtering to create intimate electrical contact. For gas sensing tests, the SWCNT film was placed on a custom-made chip-carrier and Au wires were connected between electrodes of the sensor and bonding pads of the chip-carrier using silver epoxy (DuPont 5007E). As arrayed samples enabled multiple parallel test for improvements of the selectivity and the statistical confidence [24], a multiplexer was attached to our gas sensing system for simultaneous parallel measurement (Fig. 2).

In this study, the AuNP decorated SWCNT films were loaded in a sensing chamber at a pressure of 9.4 Torr and NH$_3$ gas was introduced with dry N$_2$ as carrier gas at a constant flow rate of 100 sccm (standard cubic centimetres per minute). The electrical resistance was measured at a constant bias voltage of 0.1 V and all sensing tests were carried out at room temperature. In every measurement, the sensor was exposed to dry N$_2$ for 1 min to record initial resistance and then NH$_3$ balanced with N$_2$ was introduced for 2 min to observe the sensor response. The sensor was exposed to dry N$_2$ for 5 min to recover and this gas sensing sequence was periodically repeated four times. Imaging was performed with a Zeiss Ultra HRSEM (high resolution scanning electron microscopy) at an accelerating voltage of 3 keV. A thin film of Pt was sputtered onto the samples to avoid charging effects during SEM imaging.

3. Results and discussion

Our SWCNT films on PET substrates are transparent and flexible as shown in Fig. 1(b). The photograph shows a bent film on a PET substrate with four Au electrodes clearly visible. The inset shows a film without electrodes on a coloured background underlining its transparency.

The SEM image (Fig. 1(a)) shows a homogenous network of SWCNTs with some small bundles visible. The fine dispersion is due to our optimised spraying process and important for high conductivity and, also, for a high surface exposed for AuNP decoration. The inset shows the film after AuNP decoration. The white dots are AuNPs with a typical radius of $5 \text{ nm}$, attached to the circumference of individual SWCNTs or bundles.

The source-drain current versus source-drain voltage ($I_{sd}$ – $V_{sd}$) characteristics of a bare SWCNT film and a AuNP decorated SWCNT film are shown in Fig. 3(a). Small differences in the resistance of the SWCNT film in 2-4 probe configurations indicate the electrodes are well-defined with low contact resistances between the SWCNT network and metal electrodes as very linear $I_{sd}$ – $V_{sd}$ curves are observed. It is well-known that SWCNTs behave like p-type semiconducting materials in atmosphere, giving good contact to Ni. The resistance of all films is roughly 1.7 k$\Omega$ with an infrared transparency of $\approx 95\%$ [16]. It is important to note that the high process reliability of our SWCNT films is crucial for
The sensing performance is generally evaluated in terms of sensor response and response time. The relative variation of sensor resistance is defined as sensor response $S$ given by

$$S = \frac{R_s - R_0}{R_0} \times 100\% \tag{1}$$

where $R_s$ and $R_0$ are the resistances with and without introducing NH$_3$, respectively.

Our sensor setup enables measurements of multiple samples in parallel. As shown in Fig. 3(c), six responses from different devices on a substrate were recorded at once. Those curves show the sensor responses of the bare (lower two curves) and AuNP decorated SWCNT films (the other curves) upon 20 ppm of NH$_3$ exposure for four cycles of gas injection and recovery.

The two bare films and the four decorated films show very similar responses to the NH$_3$ injections, underlining the high reproducibility of our films. Only one of the four AuNP decorated films (denoted as Au + CNT#3) showed a less complete recovery after the first NH$_3$ injection. The AuNP decorated films show a much stronger sensitivity to the gas exposure, as the higher amplitude of $S$ indicates. This may be explained as the following.

When the bare SWCNT films are exposed to NH$_3$, it adsorbs on the surface of SWCNTs and acts as an electron-donor. It has been estimated that each NH$_3$ molecule donates 0.03–0.04 electrons with binding energy of 0.15–0.18 eV, to the nanotube [27,28]. NH$_3$ molecules effectively shift the transfer characteristics of SWCNTs to negative, thus the conductance of the SWCNTs decreases as the valance band is shifted away from the Fermi level which results in hole depletion. The sensor response to NH$_3$ has been controversial as no or low binding energy is estimated [29]. Through interaction with the hydroxyl groups on the SiO$_2$ substrate, the electronic structure of SWCNTs is considered to be indirectly influenced by NH$_3$. However, by using a PET substrate, we eliminate this contribution from SiO$_2$ substrates. Therefore, we investigated the substantial effects on the nanotube film from NH$_3$. Decorated metal nanoparticles form a Schottky-type potential barrier $\phi_p$ on semiconductor materials [25,26]. This barrier is sensitive to the metal work function which is well-known to be modified by adsorbed gaseous molecules. Though NH$_3$ molecules adsorbed onto the nanotubes are also able to modify the work function of SWCNTs, they cannot affect this interfacial potential barrier [30].

Fig. 4(a) and (b) show typical gas response curves obtained by exposing AuNP decorated SWCNT film sensors to various concentrations of NH$_3$. Even at sub-ppm level, peaks were clearly distinguishable. The sensor slowly recovers in pure N$_2$ at room temperature, thus the curves show a drift. This could be reversed by UV light illumination or annealing [31–33]. The gas response curves drastically increase ~20 s after the initial gas introduction, which is attributed to the relatively high volume of the gas sensing setup.

The sensitivity of our sensors is defined as percent resistance change between initial sensor resistance and the maximum value at the peak of the first gas sensing cycle. The AuNP decorated SWCNT films show much higher sensitivity than bare films. Metal nanoparticle decoration strongly affects the charge transfer characteristics of SWCNT as it creates localised depletion regions that act as charge scattering sites and change the potential barrier at the SWCNT-nanoparticle interface [17,18,26]. The lower conductivity of the SWCNT film upon AuNP decoration can be understood by the introduction of depletion zones through the AuNPs into the one dimensional channel of the SWCNTs [26,34]. Electron donation of adsorbed NH$_3$ molecules on the AuNPs adds electronic density and hole-electron recombination subsequently occurs after crossing over the interfacial potential barrier between the AuNP and the SWCNT, leading to a reduction of the hole current through

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**Fig. 3.** (a) Source-drain current versus source-drain voltage ($I_{ds}$ $-$ $V_{ds}$) characteristics of bare SWCNT network film (black and grey lines, respectively) and AuNP decorated SWCNT film (red line). The lower conductance of bare SWCNT film in 4-probe configuration indicates small contact resistance between SWCNT network and electrodes. The resistance of the AuNP decorated SWCNT film is higher than the bare nanotube film. (b) Bending test shows no significant conductance degradation of flexible SWCNT film for two hundred times. (c) Response curves of SWCNT film (red and blue lines) and the AuNP decorated SWCNT film (the other lines) for 20 ppm NH$_3$ gas. Light grey boxes stand for periodic introduction of 20 ppm NH$_3$ gas for 2 min. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
the SWCNT. As a result, electron-hole recombination at the potential barrier gives rise to a negative gate voltage shift resulting in improved sensor response. Whilst Schottky barriers are known to depend on work function and gas exposure, fundamental electronic interactions between SWCNTs and metal nanoparticles and the description of the potential barrier at nanoparticle interfaces are still incomplete.

The sensitivities at different gas concentrations are shown in Fig. 4(c). This time differential sensitivities are linearly proportional to the gas concentration, which allows determination of the NH$_3$ gas concentration easily. The theoretical limit of detection (LOD) of sensors can be estimated by the relative resistance change in the baseline using the root-mean-square (rms) derivation. We took about 800 data points within the first minute before gas introduction to get the initial resistance of AuNP decorated SWCNT film. The rms noise of the sensor was calculated using the following equation,

\[
\text{rms}_{\text{noise}} = \sqrt{\frac{\sum (R_{\text{sensor}} - R_0)^2}{N}}
\]

where \( R_{\text{sensor}}, R_0, \) and \( N \) are measured resistance depending on time, the initial resistance of the sensor, and the number of data points, respectively. As depicted in Fig. 4(d), signal-to-noise ratio (SNR) is linearly proportional to NH$_3$ gas concentration below 2 ppm. The amplitude of signal should be at least three times larger than the noise to be distinguishable [35]. As a result, the LOD of the AuNP decorated SWCNT sensors is 255 ± 20 ppb in our measurement setup. In fact, it was difficult to recognise peaks at 200 ppb whilst they were obvious above 300 ppb as seen in Fig. 4(b). In other words, the theoretical estimation of the sensor successfully corresponds with the experimental results.

#### 4. Conclusion

We demonstrated that transparent, flexible, and highly conductive SWCNT films on PET can be fabricated in a reproducible manner. We investigated their use as gas sensors and showed that they can act as low power NH$_3$ detectors. We demonstrated that the AuNP decoration on the transparent SWCNT films by electron-beam evaporation improved the gas sensor performance. Multiple devices measured in parallel showed similar responses. This is tentatively assigned to the modification of carrier depletion zones induced by the deposited AuNPs on the SWCNTs. They showed a fast response time to NH$_3$ but, however, did not fully recover at room temperature. A detection level on the order of 255 ppb at room temperature was derived, and a corresponding value was experimentally achieved, which is one of the lowest values reported for nanotube derived sensors.

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#### References
