



Room temperature sensor based on carbon nanotubes and nanofibres for methane detection

R.K. Roy, M. Pal Chowdhury, A.K. Pal*

Department of Materials Science, Indian Association for the Cultivation of Science, Calcutta-700 032, India

Received 23 August 2004; accepted 25 August 2004

Abstract

Carbon nanotubes and nanofibres deposited by an electrodeposition technique were utilized to fabricate sensor material for the detection of methane. Carbon nanotubes (CNT) and nanofibres were grown on Si(001) substrate using acetonitrile (1% v/v) and water as electrolyte at an applied d.c. potential ~ 20 V. Sensing properties were studied with as-deposited CNT films. It was found that the films showed good sensing properties at room temperature.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: Sensor; Carbon nanotube; Methane

1. Introduction

Development of sensors for detecting various chemical species and gases in many industrial, medicinal, environmental pollution control and commercial applications is in great need. Metal-oxide gas sensors have been the subjects of large number of investigations during the past [1–7]. The sensors based on these materials change their conductivity in the presence of oxidizing and reducing gases as electron density at the surface gets modified due to absorption and desorption of O^- , O_2^- or O^{2-} . Most of the sensors based on

oxide materials showed better and acceptable sensing behaviour at significantly higher temperatures. The growing need for the development of room temperature sensors to be used in explosive ambience like mines or petroleum fractional distillation plants ushered the rapid progress in the research and development of sensing materials which would be able to detect gases like methane at room temperature.

In this regard, carbon nanotubes (CNTs) are emerging as a promising candidate since the surface area of the CNTs is very large and there are indications that electrical properties might change at room temperature. Due to their fascinating physical and chemical properties, CNTs have emerged as ideal candidates for nanoscale devices [8–13]. Recently, applications

*Corresponding author. Tel.: +91 334 734 971;
fax: +91 334 732 805.

E-mail address: msakp@iacs.res.in (A.K. Pal).

of carbon nanotubes as oxygen [13] and methane [11] gas sensors have been reported. Ong et al. [10] described the possibility of obtaining a gas-responsive multiwall CNT–SiO₂ composite for monitoring CO₂, O₂ and NH₃. Absorption of different gases in the above composite layers changed the permittivity and conductivity of the material. Commercially available methane sensors [14,15] are based on SnO₂-based sensors and are deposited over an embedded heater. Kong et al. [13] have demonstrated the use of CNT for detecting NO₂ and NH₃. They found that exposure to NH₃ caused 100-fold depletion in conductance while exposure to NO₂ increased the conductance by almost three orders of magnitude. This was attributed to the chemical gating effect. Peng and Cho [9] proposed the concept of a new type of nanoscale sensors based on substitutional doping of impurity atoms like boron and nitrogen into intrinsic single-wall CNT.

A number of techniques are available to synthesise carbon nanotubes, most common of which are arc discharge [16], laser ablation [17] and chemical vapour deposition processes [18]. But all these synthesis techniques inherently produce carbon nanotubes along with various impurities in the form of amorphous carbon, metal catalysts and many carbonaceous particles etc. It needed further purification to produce high-quality CNTs for device applications. So the challenge still lies on the large-scale synthesis of CNTs directly onto the wafer/substrate in their purest form and in a very cost-effective way. Recently, Pal et al. [19] demonstrated that CNTs in thin film form could be deposited onto Si substrates directly by simple electrodeposition technique. This technique besides being scalable and cost-competitive would allow coating on irregular surfaces. This has ushered a new hope to develop room temperature sensors for methane detection based on CNTs.

In this report, we present the synthesis of carbon nanofibres (CNFs) by suitably changing the deposition parameters for CNT deposition [16] and the sensing properties of CNTs and CNFs deposited by electrodeposition technique onto Si substrates. Films thus produced were characterized by measuring sensing properties.

2. Experimental details

CNTs and CNFs were synthesized by electrolysis [19] using acetonitrile (1% v/v) and deionized water as electrolyte. Electrolysis was carried out at atmospheric pressure and the bath temperature was kept at ~300 K. CNTs were deposited onto Si (001) wafers (resistivity ~15Ωcm size ~10 mm × 8 mm × 0.3 mm) attached to a copper cathode. Graphite was used as the counter electrode (anode). Before mounting the substrates on the cathode, they were thoroughly cleaned and rinsed with deionized water and ethanol solution, respectively. The electrodes were separated by a distance of ~8 mm. The applied d.c. voltage between the electrodes was kept ~20 V by using a d.c. power supply capable of generating stabilized voltage (30 V, 2 A). The deposition was carried for ~4–6 hrs. The typical thickness of the films as measured by an interferometer was ~30 nm.

3. Results and discussion

By suitably changing the deposition parameters, films containing CNTs or CNFs could be deposited onto silicon substrates. SEM pictures of as-deposited CNT and CNF films are shown in Fig. 1(a) and 1(b) respectively. Formation of CNTs structures, presumably an interconnected multi-walled nanotube in a web-like network is visible (Fig. 1a). Y-type interconnected nanotubes are also visible in the films. The typical diameters of CNT bundles were 15–25 nm for the films on Si. It may be seen that the growth of CNTs on the Si surface was more or less uniform and regular and CNT films consisted of long tubes of different dimensions while the CNFs indicated (Fig. 1b) short interconnected CNTs forming a maize like topography. TEM micrographs of a CNT film are shown in Fig. 2a while the high-resolution transmission electron microscopy (HRTEM) picture of the same nanotube is shown in Fig. 2b. It may be seen that the diameter of the nanotubes is ~5 nm and the d spacing is ~0.17 nm.

The surface coverage of CNTs thus deposited was comparatively lower than that for CNFs,

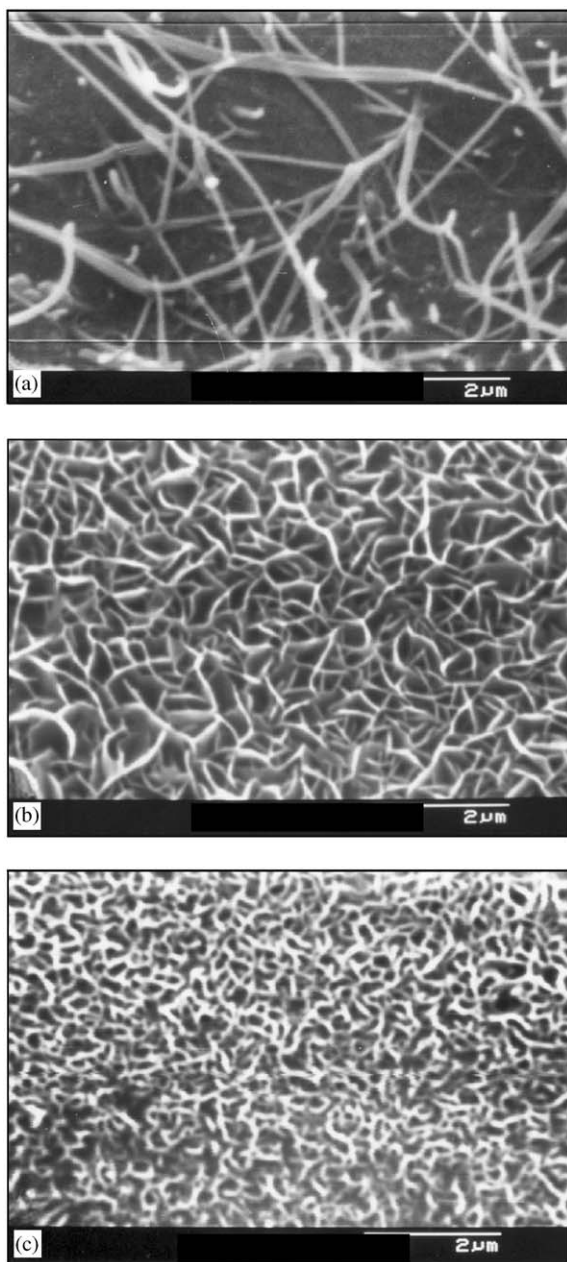


Fig. 1. SEM micrographs of three representative films: (a) as-deposited CNT film with 1% acetonitrile, (b) as-deposited CNF film with 1% acetonitrile and (c) microstructure of the films deposited 1.0% acetonitrile after gas exposure.

which increased the uncertainty of realizing electrical contacts for sensor applications with CNT films. It may be noted here that the methane

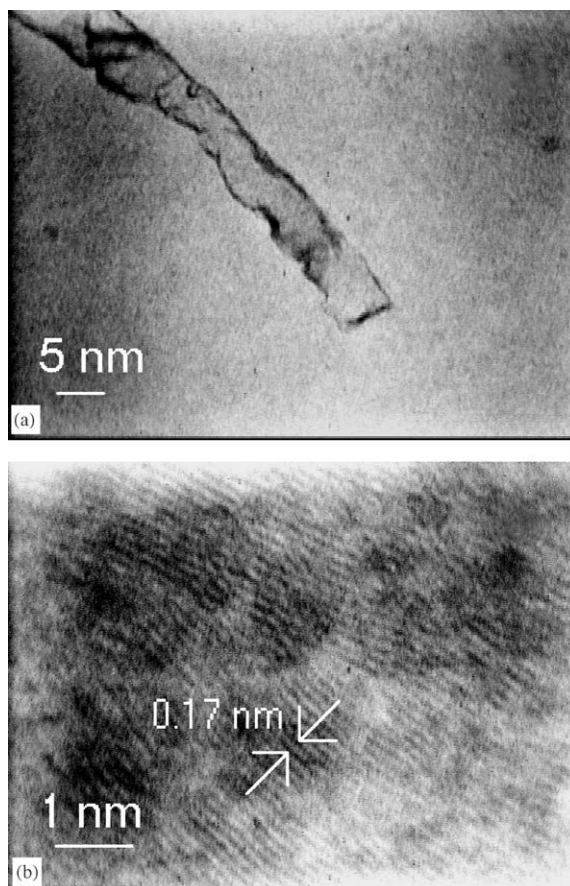


Fig. 2. (a) TEM micrograph of CNT and (b) HRTEM of the same CNT.

sensitivity of CNT films was higher (70–80%) than that obtained for CNF films (50–65%). As the reliability of obtaining very large surface coverage (90%) of the CNF deposit on the substrates was greater, it seemed that sensors based on CNFs deposits would be more technologically viable than those based on CNTs. Thus, in the subsequent sections we report our studies based on CNF films whose micrographs are shown in Fig. 1b. Thus surface coverage of the CNFs on Si substrates varied with acetonitrile concentration in the bath and the distance between the electrodes. It was found that maximum surface coverage (>90%) was obtained for films deposited from a bath containing 1% acetonitrile with the distance between the electrodes ~ 7 mm. After exposure to

methane, one may notice some changes in morphology in the interconnected CNFs. The short CNFs tended to form complete loops (Fig. 1c) rather than the random arrangements seen for as-deposited films.

The sensitivity tests were carried out in a home-made testing chamber that measures the change in surface resistance of the samples on gas exposure. The CNT and CNF films were cut into $0.5\text{ cm} \times 0.5\text{ cm}$ pieces. Electrical contacts were made out of silver pads deposited by e-gun evaporation at the two ends of the sensor element, and the terminals were connected to a multimeter (Hewlett Packard 34401A) and a constant voltage source (Advantest TR6142) for resistance measurement. The sample temperature could be controlled by a substrate heater. Argon was used as a diluting gas to achieve the ambient with the desired ppm level of methane in the chamber. The sensing characteristics of the sensor were then observed by measuring the electrical resistance change of the sensor when the latter was exposed to methane. The sensitivity $[(R_{\text{air}} - R_{\text{gas}})/R_{\text{air}}]$; R_{air} and R_{gas} being the sensor resistance in air and gas at the same temperature] defined as the percentage change of the film resistance in the presence of the test gas was calculated for each temperature and concentration of the test gas.

3.1. Methane sensing properties

Electrical contacts were made by e-gun evaporation of silver at the two ends of the CNF film. This device was mounted on a suitable heater whose temperature could be measured and controlled by a thermocouple placed on a dummy substrate placed beside the device. The whole jig was housed in a small vacuum chamber and methane diluted with argon gas, could be introduced in the chamber through an appropriate feed-through.

The possible reaction at the active surface of CNF exposed to a reducing gas ambient like methane may be understood from the following consideration. The versatility of carbon is its ability to rehybridize between sp , sp^2 and sp^3 . Also, the possibility of other intermediate degrees of hybridization are possible. This would allow the out-of-plane flexibility of graphene (a single atom-

ic layer thick sheet of graphite) for bending in form of a tube when it must lose some of its sp^2 character and gain $sp^{2+\alpha}$ character. The size of α will depend on the curvature of CNFs. Thus, the complete folding of the graphene sheet would result in the formation of a defect line having strong sp^3 character in the fold [20]. This change must involve a pair of carbon atoms due to perturbation of a double bond.

It is observed that upon exposure to methane, the CNF films became more resistive. It is known that donation of an electron pair from highest occupied molecular orbital (HOMO) of C–H bonds of methane to the p-orbitals of CNF may not be favoured as this would cause incorporation of electrons in the antibonding orbitals. It seems more probable that methane may react with CNF through CH_3^+ and H^+ added to π bonds. In this case, the hybridization state will be changed from sp^2 to sp^3 and conjugation will be lost to some extent. This would impair the electron conduction through the CNF causing an increase in resistivity.

The variation of sensitivity, as defined earlier for films deposited with different concentration of acetonitrile in the bath, is shown in Fig. 3. It may be seen that films deposited with 0.8–1.0% of acetonitrile showed higher sensitivity. This observation is in conformity with the microstructural studies discussed earlier in this paper. The surface

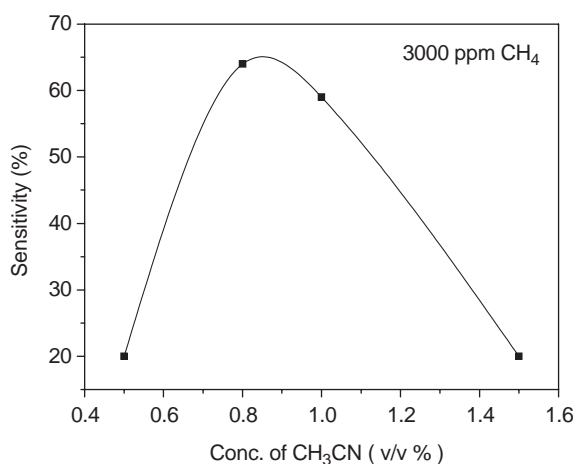


Fig. 3. Dependence of sensitivity with acetonitrile content in the bath.

coverage of the CNFs, which provided active surface area for sensing activity, decreased sharply for films deposited both at lower and higher acetonitrile concentration in the bath. Films deposited with 1% acetonitrile indicated the highest sensitivity in this study and we report all the studies on sensitivity variation based on these films.

The variation of sensitivity with methane concentration in the test chamber is shown in Fig. 4. It may be observed that the sensitivity increases more or less linearly up to 3000 ppm and then tends to saturate beyond a concentration of 4000 ppm. It seems that, due to an increase in methane concentration to 4000 ppm, more CH_3^{\bullet} and H^{\bullet} would be available to be added to π bonds. Thus, one would expect, an increase in the resistivity culminating in an increased sensitivity upto till ~ 4000 ppm of methane. With further increase in methane concentration, a marginal increase in sensitivity was observed, because there would not be sufficient number of free π bonds at the surface of CNFs available to contribute to detecting mechanism, which was reflected in Fig. 4 where the change in sensitivity was recorded for a maximum level ~ 10000 ppm of methane.

Fig 5a and b, respectively, show the variation of sensitivity with time and temperature of exposure of the films to methane. Fig. 5a shows the change in sensitivity with time when the sensor is exposed

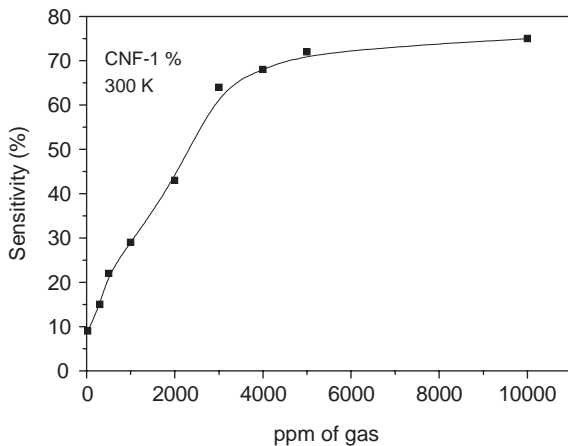
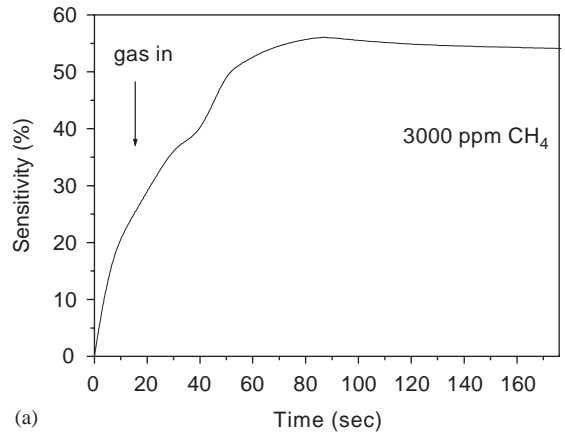
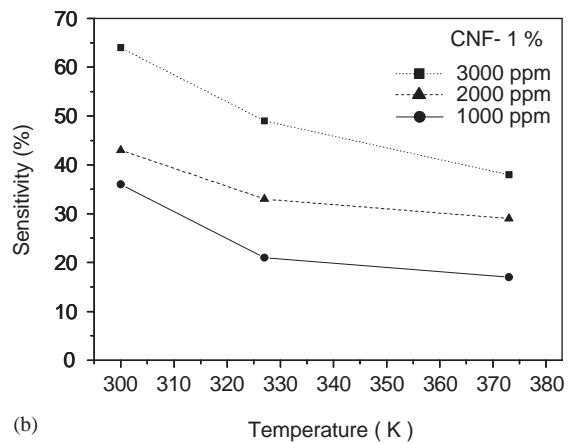


Fig. 4. Variation of sensitivity of representative films with increasing methane concentration.



(a)



(b)

Fig. 5. Variation of sensitivity with: (a) time and (b) temperature.

to methane at a level of 3000 ppm. It could be observed (Fig. 5a) that, after gas exposure, the sensitivity reaches its maximum within 80 s and does not indicate any significant change with time of exposure. The effect of increasing temperature on the sensitivity is depicted in Fig. 5b. It may be seen that the sensitivity showed a decrease with increase in temperature from 300 to 473 K. The above change in sensitivity was due to the combined effect of the increase in conductivity of the CNFs with temperature and the possible desorption of methane culminating in additional increase in conductivity. Thus, the recorded change in resistance due to gas exposure would reduce significantly as reflected in the variation of sensitivity with temperature (Fig. 5b).

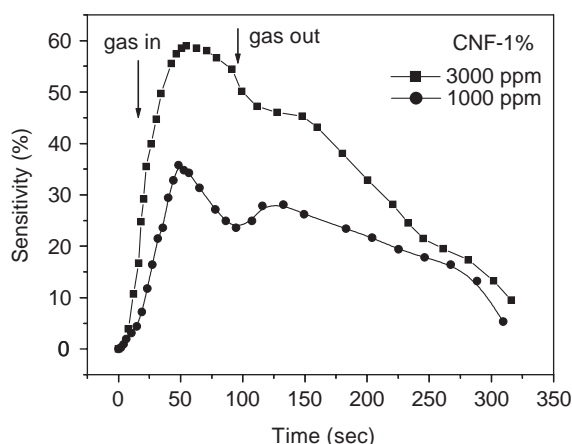


Fig. 6. Sensitivity response of the sensor.

Fig. 6 represents the variation of sensitivity with time as the test gas is introduced in the chamber. It may be seen that, in less than 50 s, the maximum sensitivity could be attained. After the withdrawal of the test gas, the sensor tends to come back to near its initial state and this change is an exponential one. The sensitivity decreases sharply for the next 50 s and then tends to decrease very slowly. The response time defines the time taken for the sensor to reach 90% of the saturation value after contact by the test gas with the surface of the sensor. The above observation suggests that the response time in these films would be ~ 45 s. It may be noted here that sensitivity was seen to decrease with repeated gas exposure. The sensitivity was found to reduce to 45% from an initial 62% after the fourth repetition. It may be stressed here that the lower cost of this sensor material CNFs and its capability to deliver 60% sensitivity at room temperature (i.e. without any embedded micro/macro heater) would make the final device a very low-cost one compared to those available in the market. Thus, using the sensing material for one-time sensing may be a viable proposition rendering the device more reliable in their use in an explosive ambient.

4. Conclusion

A room temperature sensor for methane could be obtained by depositing CNF films by a simple

electrodeposition technique. It was observed that 65% sensitivity could be observed for films deposited in a bath containing 1% acetonitrile. Sensors based on CNTs showed higher sensitivity than those based on CNF but the surface coverage of the CNF films was significantly larger than, for the CNT film rendering CNF based sensors technically more viable. The response time for these sensors was ~ 45 s.

Acknowledgements

We wish to thank Dr. P. V. Satyam, Institute of Physics, Bhubaneswar, India, for his support in recording the TEM micrographs. The authors wish to thank the Defence Research and Development Organization (DRDO), Ministry of Defence, Government of India, for sanctioning financial assistance for executing this programme. Two of us (RKR and MPC) wish to thank the award of fellowship by the Council of Scientific and Industrial Research, Government of India.

References

- [1] Salehi A. *Thin Solid Films* 2002;416:260.
- [2] Kohl D. *J Phys D Appl Phys* 2001;34:R125.
- [3] Mo Y, Okawa Y, Nakai T, Tajima M, Natukawa K. *Thin Solid Films* 2002;416:248.
- [4] Gupta S, Roy RK, Pal Chowdhury M, Pal AK. *Vacuum* 2004;75:111.
- [5] Imawan C, Solzbacher F, Steffes H, Obermeier E. *Sensors Actuators* 2000;B68:184.
- [6] Schwebel T, Fleischer M, Meixner H. *Sensors Actuators* 2002;B65:176.
- [7] Hahn S H, Barsan N, Weimar U. *Sensors Actuators* 2001;B78:64.
- [8] Li Jing, Lu Y, Ng HT, Han J, Meyyappan M. 205th Meeting, 2004, The Electrochemical Society Inc
- [9] Peng Shu, Cho K. *Nano Lett* 2003;3:513.
- [10] Ong K Ghee, Zeng K, Grimes CA. *IEEE Sensors J* 2002;2:82.
- [11] Bienfait M, Amussen B, Johnson M, Zeppenfeld P. *Surf Sci* 2000;460:243.
- [12] Cui Y, Wei Q, Park H, Lieber CM. *Science* 2001;293:1289.
- [13] Kong J, Franklin NR, Zhou C, Chapline MG, Peng S, Cho K, Dai H. *Science* 2000;287:622.
- [14] Application Notes TGS2611, Figaro Engineering Inc. Japan, 2002
- [15] Application Note MSGS-3002 Methane Gas Sensor, Microsens SA, Switzerland

- [16] Journet C, Maser WK, Bernier P, Loiseau A, Chapelle MLDeLa, Lefrant S, Deniart P, Lee R, Fischer JE. *Nature* 1997;388:756.
- [17] Thess A, Lee R, Nikolaev P, Dai H, Petit P, Robert J, Xu C, Lee YH, Kim SG, Rinzler AG, Colbert DT, Scuseria GE, Tomanek D, Fischer JE, Smalley RE. *Science* 1996;273:483.
- [18] Ge M, Sattler K. *Science* 1993;260:515.
- [19] Pal AK, Roy RK, Mandal SK, Gupta S, Deb B. *Thin Solid Films*, 2004 (in press)
- [20] Ebbesen TW, Takada T. *Carbon Nanotubes*. In: Endo M, Iijima S, Dresselhaus MS, editors. Oxford: Pergamon; 1996. p–71