www.vbripress.com/aml, DOI: 10.5185/amlett.2016.5938 Published online by the VBRI Press in 2016

Investigation of single wall nanotube gas sensor recovery behavior in the presence of UV

Deepak Kumar[1,2*], Poornendu Chaturvedi[1], Abhilasha Chouksey[1], R. P. Tandon[2] and Partap K Chaudhury[1]

[1]*Solid State Physics Laboratory, DRDO, Lucknow Road, Timarpur, Delhi 110054, India*
[2]*Department of Physics and Astrophysics, University of Delhi, Delhi 110007, India*

[*]Corresponding author. Tel: (+91) 1123903879; E-mail: kum.k.deepak@gmail.com

Received: 03 April 2015, Revised: 01 December 2015 and Accepted: 02 February 2016

ABSTRACT

The recovery of single wall nanotube (SWNT) based gas sensors have been investigated in the presence of Ultraviolet (UV) light at ambient conditions by real time monitoring. The rate of recovery is same for low concentration upto 5 ppm, but decreases with increase in concentration of NO_2. It is observed that the response of thick film resistor (CNT-TFR) remains 7.5 and 25.4 % with multiple exposures of 5 ppm and 20 ppm NO_2 concentration, respectively. But the recovery rate decreases with multiple exposures. Both the response and recovery rate changes in case of micro resistor (CNT-µR). To study the significant effect of absorbed O_2 in recovery behavior, the analyte is exposed to gas sensor with and without regeneration in the presence of UV light. The gas sensor response increases 1.5 times but it does not recover to its base line when regenerated in the presence of UV light. Copyright © 2016 VBRI Press.

Keywords: Gas sensor; adsorption; desorption; response; recovery.

Introduction

SWNT is a prominent candidate for the detection of chemicals with fast response time due to drastic resistance change in the presence of analyte [**1**]. The SWNT can detect a wide range of gases [**2-5**]. The response and recovery behavior of gas sensor are two important characteristics of a gas sensor. It is not a good sensor either one of this part is poor. The gas sensor does not give repeatable response to upcoming gas; the sensor is not able to recognize the concentration of upcoming gas. The recovery behavior is also important for sensor so that it recover to its base line after removing of gas exposure. Most of gas sensors do not recover to its baseline, there is a significant drift in baseline of gas sensor [**9**]. SWNT gas sensors also do not recover to its base line after removal of gases exposure [**1**]. The extra energy is needed in the form of heat or gate biasing or UV light for forced recovery of CNT gas sensor to base line [**1, 6-8**]. UV light is used as a source of recovery in the most of reports [**1, 2, 9**]. In previous reported papers, they studied the effect of UV light on SWNT properties and sensing response of gas sensor. Effect of oxygen on the electron transport properties has been reported using Ultraviolet desorption and thermally induced processes [**10**]. The improvement in the sensitivity and fast response has been reported using UV light treatment [**9**]. UV-light excitation gives rise to chemisorption of O_2-molecules and increases the rate of nanotube oxidation [**11**].

To the best of our knowledge, the effect of the absorbed O_2 molecule on recovery behavior of SWNT has not been studied so far by real time monitoring at ambient conditions. In this paper, we are reporting the recovery rate in the presence of UV light at ambient conditions for different exposed concentrations to gas sensor and also studied the significance of absorbed O_2 molecule on the sensor surface in recovery behavior by controlling the number of SWNT on the gas sensor and also after regeneration of the gas sensor surface.

Experimental

The gas sensors are prepared by arc discharged SWNT using powder of Carbon Solution Inc., USA. The thick film of AP-SWNT is synthesized by vacuum filtration method. The 0.5 mg of AP-SWNT is dispersed in 100 ml of 50 % DMF solution and ultrasonicated for 2h. The dispersed solution is filtered through polycarbonate membrane. A small piece of prepared film is mounted on the TO header used as gas sensor. The micro gas sensor is fabricated by aligning few numbers of SWNT between electrodes by dielctrophoresis [**5**]. The suspension of the 0.2 mg of SWMT in 100 ml of DMF is used for alignment of SWNT between electrodes. The electric field of 10v and 1MHz is applied for alignment of the SWNT. The gas sensor is mounted inside a closed gas cell for gas sensing studies and the analyte is exposed to sensor in the closed gas cell. The gas flow is controlled by an MFC controller. N_2 is used as diluting gas. Sensing measurements are carried at room temperature. TUV 8W FAM is used as a source of UV light in this experiment. The resistance measurement is done by Fluke 289 DMM. Before sensing, the sensor is soaked in N_2 flux at 4 l pm for 30 min until a saturation state established.

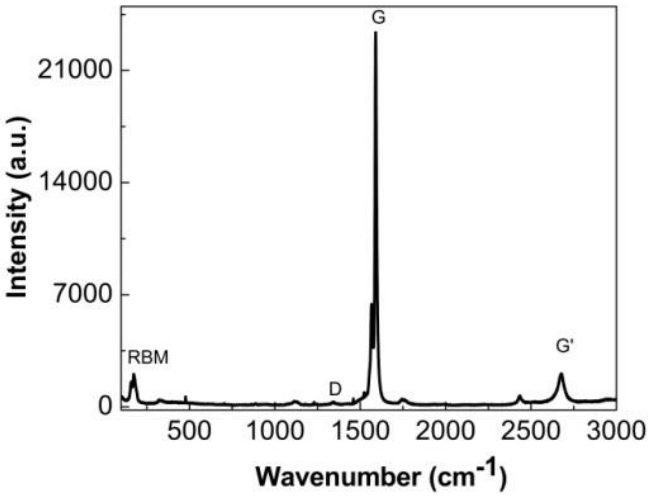

Fig. 1. Raman spectrum of SWNT.

Results and discussion

The Raman spectra of SWNT is shown in **Fig. 1** for 150-3000 cm^{-1} range. The radial breath mode (RBM) peak lies in the range 150-200 cm^{-1}. The dia of SWNT lie in the range of~1.2 to 1.8nm. The G and G′ peaks lie at 1582 and 2680 cm^{-1} [**12, 13**]. The disordered peak D lies at 1350 cm^{-1} and the ratio of I_d/I_g is 0.013, which indicates high graphitic crystallinity of SWNTs [**14**].

To study the gas sensing behavior, CNT-TFR having large number of SWNT has been taken under consideration. The random network of SWNT bundles can be observed in **Fig. 2**. The average diameter of these bundles is about 15-20 nm. The random network of SWNT provides active area for gas sensing and having large adsorbed O_2 molecules on the gas sensor surface.

The fabricated sensor is placed inside a gas cell in a constant environment of N_2. The inlet of gas cell is connected to MFC and the outlet remains open during the experiment as shown in **Fig. 3a**.

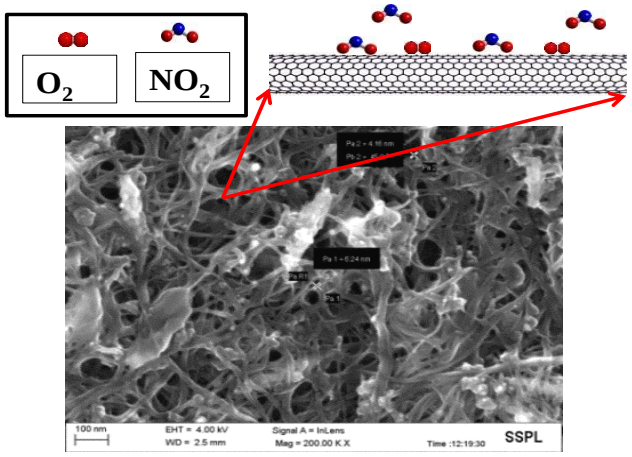

Fig. 2. SEM image of CNT-TFR film showing a random network of SWNT

Before gas sensing study, CNT-TFR is exposed to N_2. After a stable baseline in the presence of N_2, the sensor is exposed to different concentrations of NO_2 ranging from 0.5-25 ppm for 5 minutes. After switching off the exposed gas, the sensor is exposed to UV light. After recovery of gas sensor to its baseline in the presence of UV light, next cycle is exposed after 100 seconds. **Fig. 4a** shows the change in response with increasing concentrations 0.5-25 ppm of NO_2 for CNT-TFR. The response of gas sensor increases from 11.7 % to 109.2 % with increase in NO_2 concentration respectively. This change in resistance may be due to charge transfer between SWNT and NO_2. The gas sensor gives a charge of 0.3e to each NO_2 with binding energy 1eV [**15**]. SWNT gas sensor shows slow recovery and the time period of desorption is large than 12h due to high binding energy of NO_2 [**16, 17**]. To enhance the recovery rate, UV light is used as an external source of energy for desorption of NO_2 for SWNT gas sensor surface. The UV light is exposed to SWNT gas sensor in the presence of N_2 environment to protect SWNT from damage [**9**].

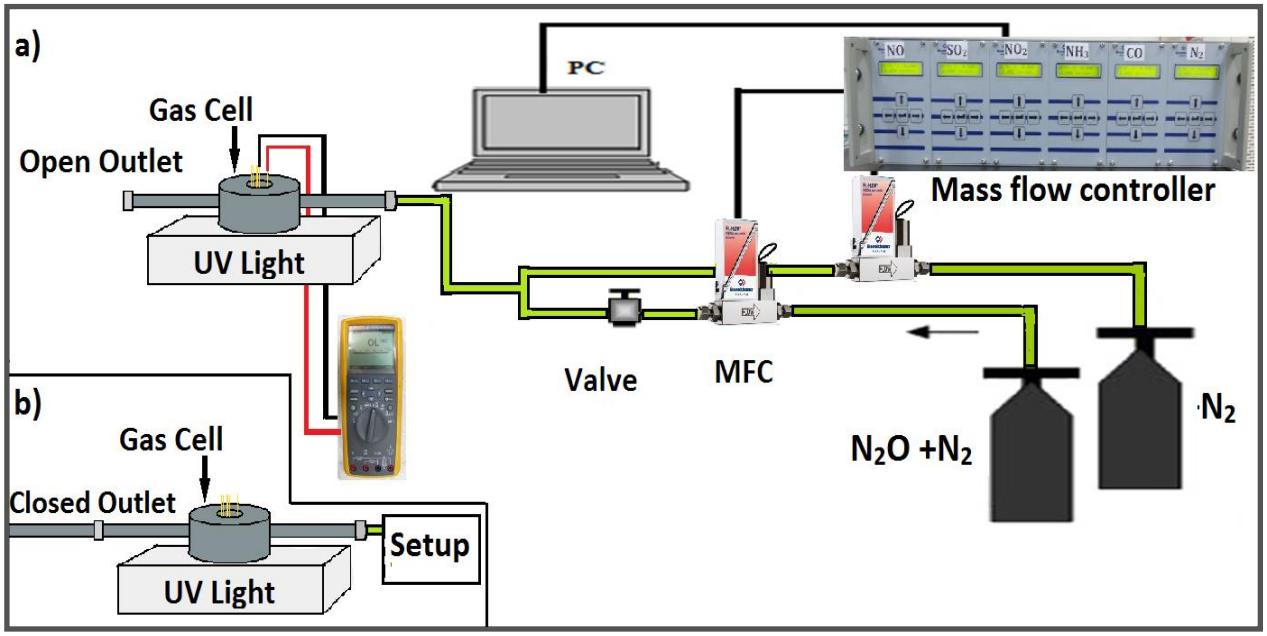

Fig. 3. Schematic diagram of Gas sensing set up. a) In first case outlet of gas sensor is open, b) In the second case the outlet of gas sensor is closed.

To study the recovery rate in the presence of UV light, the change in recovery response of the sensor with UV light is plotted (**Fig. 4b**). The resistance of gas sensor increases with UV light exposure [**9**]. This may be due to desorption of analyte from SWNT surface. It is observed from graphs that the analyte desorbs with the same rate at low concentration in the presence of UV but desorption rate changes at higher concentrations. There is a large change in gas sensor recovery rate from 10 to 25 ppm of NO_2 exposure. If NO_2 gas is desorbing in the presence of UV illuminisence, the rate of recovery should be same for all concentrations. Only the time period of recovery should increase with increase in concentration due to increase in dose of analyte exposure. But in the above case the rate of recovery has also changed with increase in desorption time on varying exposed concentration. The reason of change in recovery is discussed later. Furthermore, after switching off UV light, a remarkable feature is observed that the resistance of gas sensor decreases; hence the response of the sensor gets increased. This may be due to adsorption of the O_2 molecule on the gas sensor surface [**18, 19**]. The plot of response after UV switched off is shown in (**Fig. 4c**). The adsorption rate increases with large duration exposure of CNT-TFR to UV.

In the above study, we found that the recovery rate of gas sensor changes with long duration UV exposure. Further the effect of UV exposure on recovery rate is studied by keeping the gas concentration fixed. The gas sensor is exposed to the fixed concentration of NO_2 (5 ppm) multiple times for one minute (**Fig. 5**(**a-c**)). The gas sensor shows repeatable response of 7.5 % for 5 ppm NO_2, which means the gas sensor has approximately same empty sites for adsorption of analyte in next gas exposure. In this case gas sensor is exposed to fix the concentration of NO_2 and gas sensor recovers with the help of UV in the same condition, the rate of desorption rate should be same. It is observed that, the response of gas sensor remains same but the recovery rate changes. Something is additionally happening on the gas sensor surface with desorption of NO_2. This change may be due to desorption of another molecule from the SWNT surface with NO_2. This seems that, both NO_2 and O_2 gas desorbed from the CNT surface in the presence of UV light. The SWNT transfer 0.1e per molecule to O_2 with binding energy 0.25 eV [**20, 21**] . As O_2 has less binding energy as compared to NO_2, the O_2 desorbed at a faster rate from SWNT surface comparatively. The response of gas sensor for NO_2 is same means that molecule absorbed in every cycle is approximately same but SWNT is not able to absorb sufficient amount of O_2 as desorbed in the presence of UV light. The recovery rate of gas sensor decreased in the next cycle.

To study gas sensor recovery behavior further at higher concentration, 20 ppm NO_2 is exposed to gas sensor three times consecutively (**Fig. 5d**). The same response (25.4 %) is observed for the multiple NO_2 exposures, but the recovery rate is decreased as the number of exposure increased. This may be due to decrease in adsorbed O_2 form SWNT surface. Further, the above said studies have carried out on the number of samples showing similar type of behavior in the presence of UV light and it is found that the multiple exposure of gas sensor to UV light decreased the recovery rate of the gas sensor.

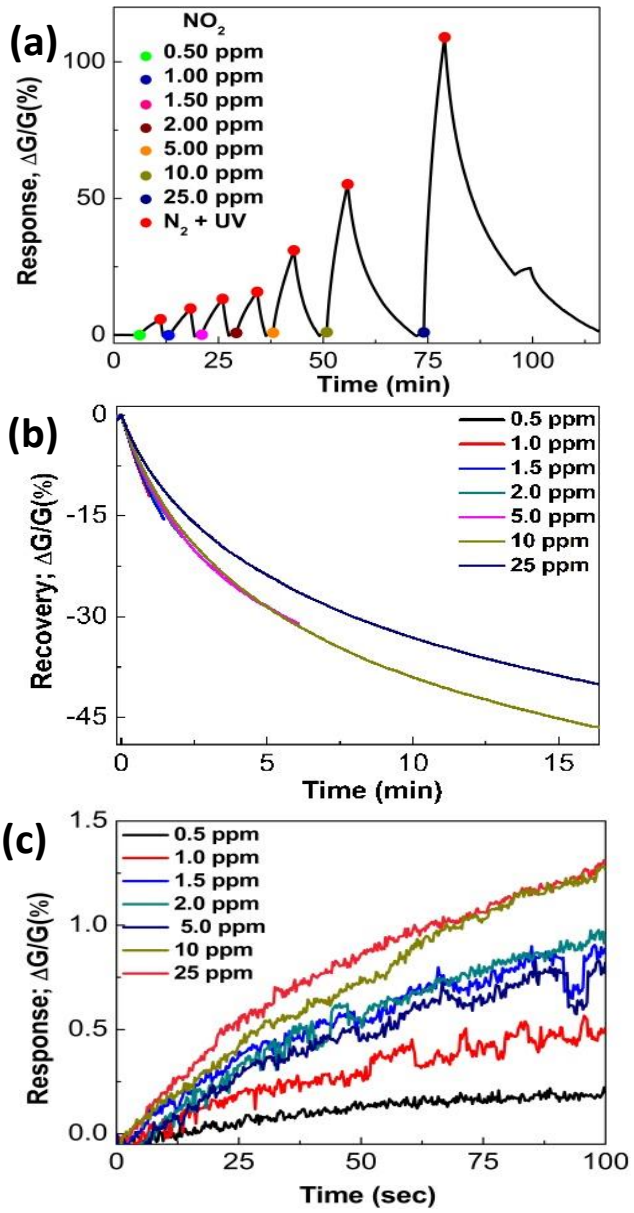

Fig. 4. a) Change in response of CNT-TFR sensor exposed to different concentration of NO_2 (0.5-25ppm), b) Shows the change in recovery rate of gas sensor with VU light. c) Shows the change in response of gas sensor after UV light is switched off.

In the above study, we found that the absorbed O_2 molecule plays an important role in recovery of gas sensor (**Fig. 6**). To study, the significance of adsorbed oxygen molecule on the SWNT surface, a microfilm SWNT gas sensor (CNT-µR) is prepared by controlling few numbers of SWNT between electrode pads. The prepared gas sensor has less number of adsorption sites due to less number of aligned SWNT bundles, hence less the adsorbed O_2 molecule. The CNT-µR is exposed to different concentration of NO_2 (**Fig. 7a**). The recovery behavior of the CNT-µR is shown in **Fig. 7b**. It shows the nonlinear behavior of CNT-µR as compared to CNT-TFR due to less number of O_2 molecules on the gas senor surface (**Fig. 7c**). Similarly to CNT-TFR, the CNT-µR gas sensor is exposed

multiple times to 5 ppm NO_2. The gas sensor shows response of 18 .6 % to the NO_2 exposure.

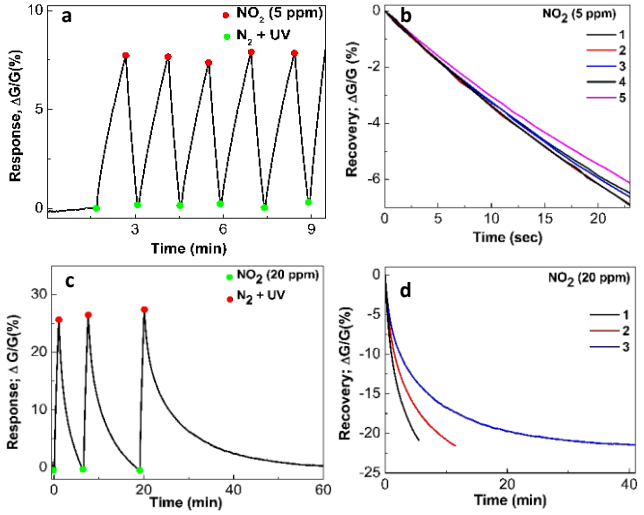

Fig. 5. a) Change in response of CNT-TFR sensor when exposed multiple times to 5 ppm NO_2. b) The recovery in the presence of UV light for 5 ppm NO_2. c) Change in response of gas sensor when exposed multiple times to 20 ppm NO_2. d) The recovery in the presence of UV light for 20 ppm NO_2.

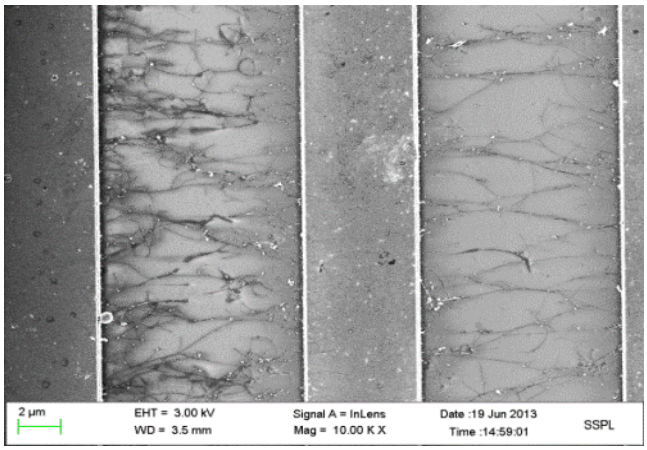

Fig. 6. The SEM image of CNT-µR showing small number of SWNT bundles aligned between the electrodes.

As it is observed in the CNT-µR response behavior (**Fig. 7d**) that the response of gas sensor is decreasing with multiple exposure of analyte. The number of adsorption sites seems to be decreased for the next cycle. This may be due to surface coverage of the analyte molecule on adsorption sites because NO_2 desorbed with slower rate as compared to O_2 molecules from the SWNT surface in the presence of UV.

To confirm the above gas sensing behaviour of CNT-µR. The gas sensor is exposed to NO_2 in the presence and absence of adsorbed O_2 molecule over CNT surface. For this experiment, the outlet of the gas cell is kept closed with a long tube as shown in **Fig. 2b**, so that no gas can diffuse from the gas cell outlet. After the closing outlet of gas cell, the gas sensor is exposed to NO_2 and then the gas sensor is exposed to UV light. The CNT-µR recovered to baseline as shown in **Fig. 8**.

To remove the adsorbed gases and O_2 molecules from the CNT-µR surface. The Gas sensor is exposed to UV in the presence of N_2 for long duration until a stable baseline is formed [**9**]. The resistance of gas sensor changes from 0.70 MΩ to 1.8 MΩ in the presence of UV light exposure. The gas sensor surface is regenerated and approximately all sites became empty for the guest molecules. After regeneration of gas sensor surface, again gas sensor is exposed to NO_2, which increased the gas sensor response to 1.5 times.

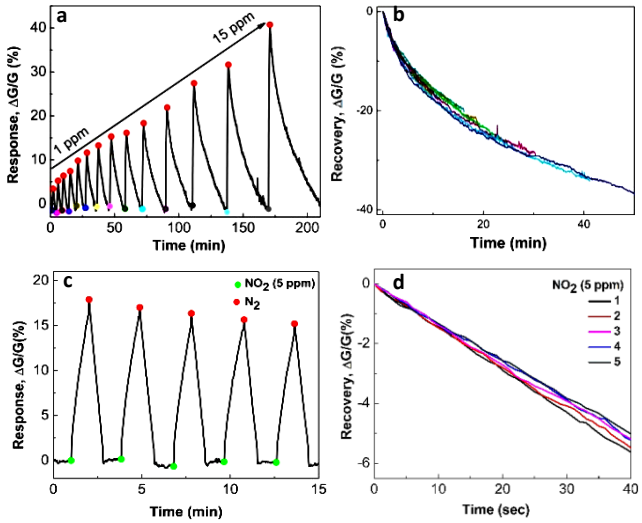

Fig. 7. a) The response of CNT-µR sensor to different concentration of NO_2 exposed, b) The recovery of CNT-µR when exposed to UV light, c) Change in response of gas sensor when exposed multiple times to NO_2 5 ppm, d) Recovery in the presence of UV light for 5 ppm NO_2.

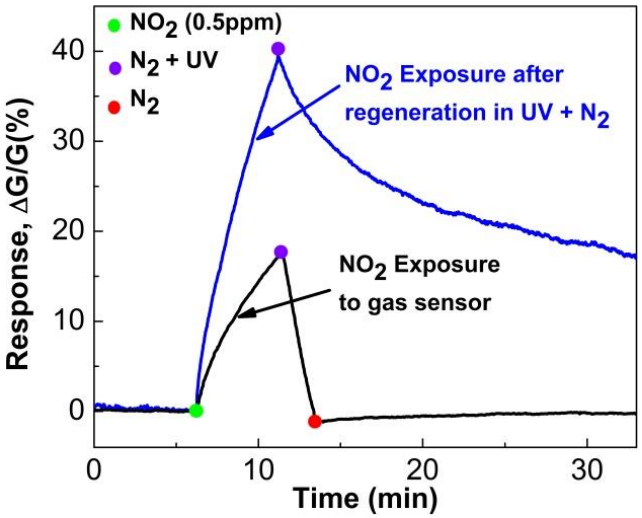

Fig. 8. Response curve for NO_2 0.5 ppm exposure to gas sensor with and without regeneration of UV light.

This may be attributed to the large number of available sites on gas sensor surface and also the recovery rate decreased in the presence of UV exposure. The gas sensor does not recover to its base line even after the UV exposure for long duration as shown in **Fig. 8**. This may be due to absence of O_2 molecule on SWNT surface. Similar behavior is found for the pristine CNT-µR. The response is increased 1.8 times for the regenerated gas sensor, but the gas sensor does not recover to baseline after regeneration.

Conclusion

In above study, we study the effect of adsorbed oxygen on the gas sensor response and recovery for repeatable response. It is observed that recovery rate is same for low concentration, but decreases with increase in concentration of NO_2 for CNT-TFR. The rate of recovery also decreases with the multiple exposures of fix concentration of analyte to CNT-TFR may be due to desorption of the O_2 molecule with NO_2 in the presence of UV light. The rate of recovery shows nonlinear behavior in CNT-µR as compared to the CNT – TFR due to less number of SWNT between electrode pads. When gas sensor surface is regenerated in the presence of UV source, the gas sensor response increases, but it does not recover to baseline. The O_2 plays an important role in the repeatable response and recovery of the SWNT gas sensor. This study helps for repeatable response of the SWNT gas sensor.

Acknowledgements

Authors gratefully acknowledge Dr. R. K. Sharma, Director, Solid State Physics Laboratory for the guidance and permission to publish the work and one of the authors (D.K.) thankful to DRDO, for providing a research fellowship.

Reference

1. Li, J.; Lu, Y.; Ye, Q.; Cinke, M.; Han, J. and Meyyappan, M.; *Nano Letters*, **2003**, *3*, 929. **DOI:** 10.1021/nl034220x
2. Wang, Y. and Yeow, J. T. W.; *Journal of Sensors*, **2009**, 2009. **DOI:** 10.1155/2009/493904
3. Asad, M.; Sheikhi, M. H.; Pourfath, M. and Moradi M.; *Sensors and Actuators B: Chemical*, **2015**, *210*, 1. **DOI:** 10.1016/j.snb.2014.12.086
4. Chaste, J.; Eichler, A.; Moser, J.; Ceballos, G.; Rurali, R. and Bachtold, A.; *Nat. Nanotechnol.*, **2012**, *7*, 301. **DOI:** 10.1038/nnano.2012.42
5. Zhang, T.; Mubeen, S.; Myung N. V. and Deshusses, M. A.; *Nanotechnology*, ***2008***, *19*, 33200. **DOI:** 10.1088/0957-4484/19/33/332001
6. Cho, W. S., Moon, S.; , Paek, K. K.; Lee, Y.H. ; Park, J. H.; Ju, B. K.; *Sensors and Actuators B: Chemical*, **2006**, *119*, 180. **DOI:** 10.1016/j.snb.2005.12.004
7. Ueda,T.; Bhuiyan, M. M. H.; Norimatsu, H.; Katsuki, S.; Ikegami, T. and Mitsugi, F.; *Physica E: Low-dimensional Systems and Nanostructures*, **2008**, *40*, 2272. **DOI:** 10.1016/j.physe.2007.12.006
8. Moon, S. I.; Paek, K. K.; Lee, Y. H.; Park, H. K.; Kim, J. K.; Kim, S. W. and Ju, B. K.; *Materials Letters*, **2008**, *62*, 2422. **DIO:** 10.1016/j.matlet.2007.12.027
9. Chen, G.; Paronyan, T. M.; Pigos, E. M. and Harutyunyan, A. R.; *Scientific Reports* **2012**, *2*, 343. **DIO:** 10.1038/srep00343
10. Shim, M.; Back, J. H.; Ozel, T. and Kwon, K. W.; *Phys. Rev. B*, **2005**, *71*, 205411. **DOI:** 10.1103/PhysRevB.71.205411
11. Grujicic, M.; Cao, G.; Rao, A. M.; Tritt, T. M. and Nayak, S.; *Applied Surface Science*, **2003**, 214, 289. **DOI:** 10.1016/S0169-4332(03)00361-1
12. Dresselhaus, M. S.; Dresselhaus, G.; Saito, R. and Jorio A.; Physics Reports, **2005**, *409*, 47. **DOI:** 10.1016/j.physrep.2004.10.006
13. Cantalini, C.; Valentini, L.; Lozzi, L.; Armentano, I.; Kenny, J. M. and Santucci, S.; *Sensors and Actuators B: Chemical*, **2003**, *93*,333. **DOI:** 10.1016/S0925-4005(03)00224-7
14. Hussain, S.; Jha, P.; Chouksey, A.; Raman, R.; Islam, S. S.; Islam, T.; Choudhary, P. K. and Harsh; *Journal of Modern Physics*, **2011**, *2*, 538. **DOI**: 10.4236/jmp.2011.26063
15. Peng, S.; Cho, K.; Qi, P. and Dai, H.; *Chemical Physics Letters*, **2004**, *387*, 271. **DOI:** 10.1016/j.cplett.2004.02.026
16. Kong, J.; Franklin, N. R.; Zhou, C.; Chapline, M. G.; Peng, S.; Cho, K.; Dai, H.; *Science*, **2000,** 287622. **DOI:** 10.1126/science.287.5453.622.
17. Wang, L. C.; Tang, K. T.; Teng, I-J.; Kuo, C. T.; Ho, C. L.; Kuo, H. W.; Su, T. H.; Yang, S. R.; Shi, G. N. and Chang, C. P.; *Sensors*, **2011**, *11*, 7763. **DOI**: 10.3390/s110807763
18. Tchernatinsky, A.; Desai, S.; Sumanasekera, G. U.; Jayanthi, C. S.; Wu, S. Y.; Nagabhirava, B.and Alphenaar, B.; *J. Appl. Phys*., **2006**, *99*, 034306. **DOI:** 10.1063/1.2163008.
19. Huang, C. S.; Yeh, C. Y.; Yuan, C. H.; Huang, B. R. and Hsiao, C. H.; *Diamond & Related Materials*, **2009**, *18*, 461. **DOI**: 10.1016/j.diamond.2008.11.019
20. Jhi, S. H.; Louie, S. G. and Cohen M. L.; *Phys. Rev. Lett*. **2000**, *85*, 1710. **DOI:** 10.1103/PhysRevLett.85.1710.
21. Giannozzi, P.; Car, R. and Scoles, G.; *J. Chem. Phys*., **2003**, *118*, 1003. **DOI:** 10.1063/1.1536636.

.

