Devices and sensors based on PVDF-TrFE/SWNT's composites

Manuel Bonilla, Idalia Ramos and Nicholas Pinto
University of Puerto Rico-Humacao
Humacao PR 00972
manuel.bonilla@upr.edu

Abstract

Sensor devices were prepared using PVDF-TrFE/SWNT's composite and compared with a pure SWNT's sensor. Current as function of time measurements at room temperature shows an improved sensitivity and faster response time in the presence of acetone for the composite resistor device that was fabricated putting the composite solution between two gold electrodes on an *n* doped Si/SiO_2 substrate. The pure SWNT's resistor produced a faster response time that the composite in the presence of NO_2. Schottky diodes were prepared with the PVDF-TrFE/SWNT's composite and the *n* doped Si/SiO_2 substrate. Successful rectification was obtained and changes in the turn on voltage and in the I_{on}/I_{off} ratio were observed as the diode was in the environments of different gases. The composite improved the sensitivity of the devices that are faster and can be used to prepare a device with both diode and resistor functionalities. These sensor and the diodes can be reused after the removal of the gases.

Keywords: PVDF-TrFE, SWNT's, diode, sensor

Introduction

Nanofibers and nanotubes have a large surface to volume ratio. This feature is especially useful in sensor technology as the sensor response will be rapid. Single walled carbon nanotubes (SWNT) have been used to sense various gases and show high sensitivity [1]. We have focused our research on the composite ferroelectric co-polymer poly (vinylidene fluoride-trifluoroethylene)-PVDF-TrFE (75/25) with SWNT's. Sensors and a Schottky diode were fabricated using cast films of this composite material and tested in the presence of acetone and NO_2. The sensor response was rapid and reversible. The ability to sense NO_2 at room temperature is particularly useful as many ceramic sensors can only sense this gas at elevated temperatures. The diodes show rectification that was tunable in the presence of the gas and was reusable upon removal of the sensing gas.

Experimental

Devices were prepared using a 1 wt% solution of SWNT's dispersed in N,N-Dimethylformamide (DMF) and a solution of 1 wt% PVDF-TrFE in DMF for the composite devices. These solutions were drop cast on *n*-doped Si/SiO_2 wafer (<0 0 1>, 0.1-1.0 Ω cm) with a 200nm thermally grown oxide layer. The PVDF-TrEF/SWNT's composite was a mixture of 0.5 ml of SWNT's in DMF and 4.5 ml of 1 wt% PVDF-TrFE in DMF For sensor measurements, the current at fixed voltage was measured as a function of time for resistor devices of pure SWNT's and the composites. These measurements were taken in the presence of NO_2 and in the presence of acetone using N_2 as the inert carrier gas. Schottky diodes consisting of pure SWNT'S/*n*-Si and also of the composite/*n*-Si were prepared and electrically characterized under the same gaseous conditions

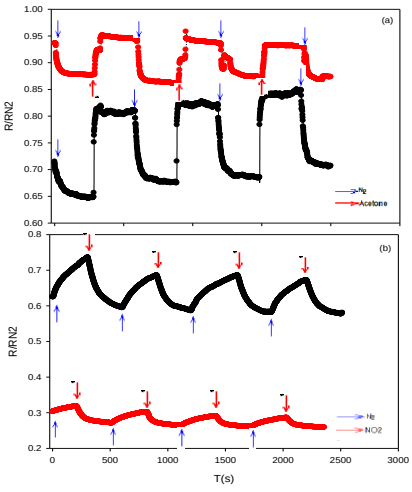

Fig. 1.Normalized resistance of individual sensors switching the gas ambience between (a) N_2 and acetone (b) N_2 and NO_2. PVDF-TrFE/ SWNT's *is in black and* SWNT's. *in red. The arrows indicate the moment when the specified gas was introduced*

Table 1
Composite and pure SWNT's sensors response time and recovery time

Sample	PVDF-TrFE/SWNT's		SWNT's	
Sensing gas	Acetone	NO_2	Acetone	NO_2
Response time(s)	5	200	15	180
Recovery time (s)	100	235	120	200

Results and discussion

Figure 1 shows the normalized resistance of the pure SWNT and the composite PVDF-TrFE/SWNT sensors in the presence of acetone and NO_2 gases. The response to acetone is rapid and true saturation can be observed, while for NO_2 the sensor does not appear to saturate in the 300s time interval of the measurements. Nevertheless, in the four cycles presented in Figure 1, there is reproducibility. The response times of these sensors is presented in Table 1 and shows that composite sensors are much faster than pure SWNT sensor for acetone. This could be due the presence of the polymer that speeds gas entry into the fiber. From Figure 1 we see that acetone increases the resistance due to polymer swelling while NO_2 decreases it and could be related to the doping effect that NO_2 has on organic materials eg. graphene [2].

Figures 2(a) and (b) show the I-V characteristic curves for the Schottky diode made of composite PVDF-TrFE/SWNT's in the presence of acetone and NO_2 respectively and Figures 2(c) and (d) show the same for the pure SWNT's under the same conditions. In all these figures we notice the asymmetric rectifying behavior. Consistent with the sensor measurements in Figure 1, acetone reduces the on state current, the effect of NO_2 is more pronounced in the reverse bias direction. In all cases however we notice the diode recovers after the sensing gas is removed making useful as a reusable diode cum gas sensor. The performance of the diode was analyzed using the standard thermionic emission model of a Schottky junction via the equations above and device parameters are tabulated in Table 2.

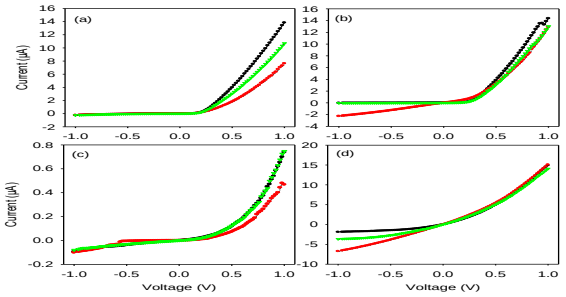

Fig. 2.Current-voltage characteristic of the Schottky diodes. The black plots are under the presence of N_2.The red plots corresponds to a ambience of (a) acetone (b) $N0_2$ for the composite diode and (c) acetone (d) NO_2 for the CNT's diode. The green plots are after the removal of the gas.

$$J = J_S[\exp\left(\frac{qV_B}{kT}\right) - 1]$$

$$J_s = A^*T^2\exp\left(-\frac{q\Phi_B}{kT}\right)$$

$$n = \frac{q}{KT}\left(\frac{\partial V_B}{\partial lnJ}\right)$$

Table 2
The turn on voltage (V_{on}), I_{on}/I_{off} ratio, the diode ideality factor and the barrier height

Sensing gas	V_{on}	I_{on}/I_{off}	n	Φ_B (eV)
PVDF-TrFE/CNT's in Acetone				
N_2	0.30	57	1.7	0.46
Acetone	0.39	34	1.6	0.45
PVDF-TrFE/CNT's in NO_2				
N_2	0.37	550	2.3518	0.44
NO_2	0.27	6	4.462	0.35
CNT's in Acetone				
N_2	0.55	8	4.5	0.4453
Acetone	0.56	5	2.4	0.5065
CNT's in NO_2				
N_2	0.31	8	3.3	0.34
NO_2	0.27	2	5.0	0.32

Conclusion

Sensors based on pure SWNT's and PVDF-TrFE/SWNT were fabricated and tested in acetone and NO_2. The composite sensors had a faster response time in acetone compared to NO_2. A Schottky diode was also prepared using these same materials and the device retained its rectifying behavior in the presence of the sensing gas and there is recovery upon gas removal.

Acknowledgments

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References

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