Pressure Sensitive Organic Sensor Based on CNT-VO₂(3fl) Composite
(Pengesan Organik Sensitif Tekanan Berasaskan Komposit CNT-VO₂(3fl))

ADAM KHAN, KH. S. KARIMOVA, ZUBAIR AHMAD*, KHAULAH SULAIMAN, MUTABAR SHAH & S.A. MOIZ

ABSTRACT

In this paper, fabrication and investigation of organic pressure sensor based on Al/CNT-VO₂(3fl)/Cu composite is reported. The active layer of the composite was deposited by drop-casting of the blend CNT-VO₂(3fl) on a glass substrate (with prefabricated copper (Cu) electrode). The thin film of the blend consists of carbon nanotube CNT, (2.55 wt. %) and vanadium oxide (VO₂(3fl)) micropowder, (3 wt. %) in benzol (1 mL). The thickness of the composite was in the range of 20-40 μm. It was found that the fabricated sensor was sensitive to pressure and showed good repeatability. The decrease in resistance of the sensor was observed by increasing the external uniaxial pressure up to 50 kNm². The experimentally obtained results were compared with the simulated results and showed reasonable agreement with each other.

Keywords: Carbon nanotube; pressure sensor; resistance; vanadium oxide

INTRODUCTION

Electronic devices based on organic semiconductor materials have attracted researchers from the last decades due to low cost and large area electronic applications (Abdullah et al. 2012; Darlinski et al. 2005; Dimitrakopoulos & Malenfant 2002). Organic semiconductor materials have been employed as an active material in different electronic devices such as organic light emitting diodes (OLED), organic thin film transistors (OTFT), strain sensors, pressure sensors, humidity sensors and organic solar cells (Ahmad et al. 2011, 2008; Aziz et al. 2010; Jung et al. 2007; Mizukami et al. 2006; Stewart et al. 2001). For sensing applications new organic materials and their composites have been studied (Darlinski et al. 2005; Dimitrakopoulos & Malenfant 2002; Jung et al. 2007; Mizukami et al. 2006; Shah et al. 2012; Stewart et al. 2001).

Pressure sensors are used for controlling and monitoring of pressure in thousands of everyday applications. Pressure sensors are mostly fabricated on the basis of piezo-resistive, capacitive, inductive and piezoelectric elements (Dally et al. 1983; Simpson 1996). Someya et al. (2005) fabricated a network of pressure sensors with organic transistors based on pentacene. The drain-source current was increased from 15 nA to 6.7 μA, under an applied pressure of 30 kPa. Piezoelectricity and electrostriction were observed in organic semiconductor Schottky junctions due to the presence of non-uniform spatial electric field distribution in the junction and softness of organic semiconductors. This effects can be potentially used for the fabrication of electromechanical sensors (Dennler et al. 2005).

Carbon nanotubes (CNTs) are also interesting due to their unique electronic and mechanical properties. Electronically, CNTs can be metallic, semiconducting or small-gap semiconducting (SGS) materials, depending on the orientation of the graphene lattice with respect to the axis of the tube (Grow et al. 2005). Different kinds of sensors have been fabricated and investigated on the basis of CNTs (Saleem et al. 2010; Shah et al. 2012; Tang et al. 2006; Varghese et al. 2001).

The electromechanical properties of the CNTs are interesting and could lead to their use as piezo-resistors in mechanical sensors such as strain gauges, pressure sensors and accelerometers. The piezo-resistance of CNTs on deformable thin-film silicon nitride membranes was investigated (Grow et al. 2005) and it was found that the gauge factors (AR/Re) were 400 and 850 for the semiconducting and SGS tubes, respectively, whereas the maximum value of a gauge factor in silicon was 200.
The small band-gap semiconducting (or quasimetallic) nanotubes were investigated and it was found that they exhibit the piezoresistive gauge factors from 600 to 1000 under axial strains, which are much larger than in metallic nanotubes (Cao et al. 2003). The fabrication of SWNT thin-film transistors on plastic substrates was described (Xue & Cui 2008). It was shown that the resistance of the SWNT thin film decreases to 38.2, and 47.1% with an increase of the bending of the elastic substrate for the thin films containing 14 and 16 SWNT layers, respectively, which were 10 times higher than silicon. It was demonstrated that the piezoresistive effect in the pristine CNTs films; at room temperature, the gauge factor under 500 microstrains was 65 (Li et al. 2003). The gauge factor increased with temperature. Mechanical deformation-conductivity relationships of freestanding membranes of SWNTs have been investigated (Regoliosi et al. 2004) and it was shown that the nanotubes gauge factor of piezoresistivity is 2.3-2.5 times larger than that of the silicon substrate. The nano electromechanical piezoresistance transducers based on SWNTs were investigated and it was shown theoretically and experimentally that ballistically conducting SWNTs show nonlinear piezoresistive gauge factors of up to 1500 (applied strain was 1%) (Stampfer et al. 2007).

Vanadium oxide (\(\text{VO}_2\)) shows the large reversible change of electric, magnetic and optical properties at temperatures around 68-70°C (Guzman 2000). In the infrared spectrum of this material, transmission of semiconductor to metal is observed. At transition temperature, optical properties of vanadium dioxide were quickly changed; the optical transmission is decreased and reflectivity is increased. Due to this behavior vanadium dioxide is an attractive material for solar energy control and electrical and optical switches. Microstructure and crystallinity of the films effect hysteresis of the transition. By the addition of transition metals such as niobium, molybdenum or tungsten, the transition temperature of vanadium dioxide may be decreased.

Fabrication of the pressure sensor and investigation of the squeezing effect on the CNT-\(\text{VO}_2\) (3fl) film would be useful from a practical point of view and for deepening of the knowledge about the physical properties of the composite. The electrical characteristics of \(\text{VO}_2\) (3fl) have also been investigated by (Karimov et al. 2011). It would be reasonable to investigate the resistance-pressure relationships. In this paper we have designed, fabricated and investigated the sandwich-type pressure resistance sensors based on CNT-\(\text{VO}_2\) (3fl) composite.

**EXPERIMENTAL DETAILS**

The CNTs and \(\text{VO}_2\) (3 fl) micro-powder were commercially purchased from Sun Nanotech Co Ltd. China and Sigma Aldrich, respectively and was used without further purification. The glass substrates of thickness of 2 mm were cleaned with acetone. Afterwards, copper was deposited as the bottom electrode on these substrates. The blend of vanadium oxide micropowder \(\text{VO}_2\) (3fl), (2.5 wt. %) and CNT (2.5 wt. %) in benzol (1 mL) was drop-casted on the glass substrates to fabricate \(\text{VO}_2\)-CNT microcomposite thin films. The thicknesses of the CNT-\(\text{VO}_2\) (3fl) films were in the range of 30-40 μm. As a top electrode thin aluminum foil of thickness 40 μm and size of 5 x 5 mm was used to make the sandwich-type resistance pressure sensor based on CNT-\(\text{VO}_2\) (3fl) (Figure 1). Figure 2 shows the experimental setup for the investigation of pressure sensor’s properties. The setup consists of the following elements: support (1), weight holder (2), weights (3), metallic squeezing disk (4) of diameter 8 mm and elastic rubber film (5) of 0.5 mm thickness. The pressure sensor (6 is aluminum foil, 7 is CNT-\(\text{VO}_2\) (3fl) composite film, 8 is glass substrate, 9 is support, 10 and 11 are terminals) is placed between the support and the rubber film. The value of the pressure was changed by changing the values of the weights. The main parts of the experimental setup i.e. weight holder and weights were used from the conventional laboratory setup Flexor: Cantilever flexure frame. The DC resistance was measured by FLUKE 87 true rms multimeter at room temperature.
RESULTS AND DISCUSSION

Figure 3 shows the resistance-pressure relationships for one of the CNT-VO$_2$ (3f) sensors during increase and decrease in pressure. It was observed that the resistance of the sensor decreases with increase in pressure. It was also noted that while decreasing the pressure (unloading), practically there is less hysteresis. The sensor’s resistance ($R$) can be represented by the following expression (Irwin & Nelms 2007):

$$R = \frac{dp}{A} = \frac{d}{\sigma A},$$  \hspace{1cm} (1)

where $d$ is the length or the inter-electrode distance, $A$ is the cross-section of the sample, and $\rho$ is the resistivity ($\rho = \frac{1}{\sigma}$, where $\sigma$ is conductivity). As CNT-VO$_2$ (3f) system is a microcomposite, the change in resistance to applied pressure (Figure 3) may be due to the change in geometrical parameters or intrinsic properties of the sample. In most semiconductors, the change in resistivity is of several orders greater than the change in geometrical parameters of the sample; hence, change in resistance of the materials is mainly attributed to the resistivity change of the sample rather than its geometrical parameters (Schols 2011). Hence, it may be assumed that the latter process is dominating.

Figure 4 shows the relative resistance-pressure relationships for the two samples. It was observed that the effect of pressure at thicker sample was more significant as compared with the thinner sample. The transfer function of the sensor as depicted from Figure 3 was simulated as an exponential function (Karimov et al. 2010):
\[ f(x) = e^{-x}. \]  

In this case, the (2) can be written as:

\[ \frac{R}{R_0} = e^{-Ke}. \]

where \( p \) is pressure, \( K \) is the resistance pressure factor and \( R_0 \) is the initial resistance of the sensor at no pressure. The value of \( K \) can be computed from the experimental data shown in Figure 3 and was found as 0.022 kN^{-1} m^2. For the best match of simulation and experimental results, we modified the above (3) as:

\[ \frac{R}{R_0} = e^{-\frac{10p_{m}Ke}{Z_{m}+p_{m}Ke}}, \]

where \( p_{m} \) is the maximum applied pressure and \( K_{m} \) is the maximum resistance pressure factor at maximum pressure. Figure 5 shows the comparison between simulated and experimental results and were found in good agreement.

In multicrystalline disordered semiconductors due to localized states, mostly phonon assisted hopping transport of charge transport is observed between spatially distributed sites (Brabec et al. 2003). In hopping, charges hop out from one localized state to another and contribute to conductivity. The conductivity of charges in this random geometry is attributed to percolation theory. According to this theory, the average conductivity of one component (let say CNT) can be calculated using this expression:

\[ \sigma = \frac{1}{LZ}. \]

where, \( L \) is the characteristic length between sites and \( Z \) is the average resistance of the connecting path between sites. As pressure is applied to the sample, due to squeezing effect the concentration of charges at sites increases, which reduces the average resistance \( Z \) between the sites. Also the characteristic length decreases among neighboring sites. Consequently, the conductivity of overall sample increases and the resistance of the composite decrease, accordingly, as observed experimentally (Figure 3). Secondly, below the localized state there exists a trap state and in this region charges are not able to cross the potential barrier. Hence, the charge transport in disordered organic semiconductors is limited by these deep potential wells. When a charge carrier is trapped, it may not cross the potential barrier and hence did not take part in conductivity. As the concentration of charges increases under the squeezing effect, the trap regions may become filled, therefore, minimizing the trap effect and increases the conductivity of the sample. The log relative resistance-pressure relationship is plotted in Figure 6. It was seen that the graph is quasi-linear. It means that the original graphs can be linearized by the nonlinear op-amps that are important for practical application of the sensors.

**CONCLUSION**

The sandwich-type Al/CNT-VO_2 (3fl)/Cu pressure sensor was designed, fabricated and investigated. The resistance-pressure relationships were simulated. The resistance of the sensor was observed to decrease as the pressure was increased. For the explanation of the conduction mechanism, the percolation theory is used. The CNT-VO_2 (3fl) system is assumed as a bulk hetero-junction system that results in high sensitivity of the composite due to the squeezing effect.

**ACKNOWLEDGEMENTS**

We thank the Ministry of Education (MOE), Malaysia for the financial support under Fundamental Research Grant (FRGS) No. FP007/2011A.
Figure 6. Log relative resistance - log pressure relationship for the CNT-VO₂(3fl) based sensor

REFERENCES


Adam Khan & Kh. S. Karimov  
GIK Institute of Engineering Sciences & Technology  
Topi 23640, KPK  
Pakistan  

Mutabar Shah  
Institute of Physics and Electronics  
University of Peshawar  
25120, Peshawar, KPK  
Pakistan  

Zubair Ahmad & Khoulah Sulaiman  
Low Dimensional Materials Research Center  
Department of Physics  
University of Malaya  
50603 Kuala Lumpur  
Malaysia  

S. A. Moiz  
Department of Electrical Engineering  
Faculty of Engineering & Islamic Arch.  
Umm-ul-Qura University  
P.O Box: 5555, Makkah  
Saudi Arabia  

*Corresponding author; email: zubairtarar@um.edu.my  

Received: 1 April 2013  
Accepted: 31 December 2013