Materials Science in Semiconductor Processing 41 (2016) 26–31

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Effect of physicochemical properties of analyte on the selectivity of polymethylmethacrylate: Carbon nanotube based composite sensor for detection of volatile organic compounds

Amandeep Kaur [a,*], Inderpreet Singh [b], Amit Kumar [c], Peta Koteswara Rao [a], Pramod Kumar Bhatnagar [a]

[a] Material Science Laboratory, Department of Electronic Science, University of Delhi South Campus, Benito Juarez Road, New Delhi 110021, India
[b] Department of Electronics, SGTB Khalsa College, University of Delhi, Delhi 110007, India
[c] Department of Electronics, BCAS, University of Delhi, New Delhi 110075, India

ARTICLE INFO

Article history:
Received 1 June 2015
Received in revised form
4 August 2015
Accepted 4 August 2015

Keywords:
Selectivity
Methanol
Molecular size and electronegativity

ABSTRACT

We report for the first time, the effect of physicochemical properties of analyte on the selectivity of the polymethylmethacrylate: functionalized Multiwalled carbon nanotubes (PMMA: f-MWCNTs) composite sensor. In the present work, we have developed an optimized composite sensor and its selectivity was studied in detail. The sensor was exposed to various organic vapors and their response, response time and recovery time were recorded. It was found that the selectivity is jointly governed by the electronic and structural properties of both the species i.e. the sensing material and the vapor molecule. Also the discrimination towards different organic vapors strongly depends on the adsorption and chemical properties of the analyte. The sensor was observed to be highly selective for methanol vapor owing to its smallest molecular size and highest electronegativity.

1. Introduction

Carbon nanotube (CNT) is a widely studied nanomaterial for the detection of volatile organic compounds (VOCs) due to their several advantages such as high surface to volume ratio, high electrical conductivity, tendency to tailor their electronic band gap structure in accordance with the ambient conditions and capability to adsorb organic compounds on their surface [1–5]. In the past few years, various researchers have developed gas sensors by incorporating CNTs in the polymer matrix due to their enhanced sensing characteristics. The important advantage of the polymer composites is that they are cost effective, can be easily shaped, withstand high temperatures, consume less power, exhibit fast response and are mechanically resistant [6–9]. The thin film structures of the composite have found application in early detection as they can be embedded in or near the source of organic vapors in the form of composite tapes that can be fixed on pipes or fuel tanks to detect any leakage. These composites have also found application in enhancing the shelf life of food material by absorbing any unwanted vapor in the surroundings [10].

The literature survey shows that different polymer matrices exhibit selective behavior for different type of organic vapors [11]. It has also been observed by some workers that the concentration of CNTs has to be optimized for better sensing response [12]. By employing polyethylene oxides as polymer matrix, Razak et al. [13] have shown that the sensitivity of the composite film is also influenced by the alignment of nanotubes in the polymer.

Although these researchers have worked on different properties of the composite based sensor for developing an efficient sensor, but the major issue faced by them is the dispersion of CNTs into individual nanotube structures. This is due to the fact that the entangled nanotube bundles inhibit the performance of the devices based on it. The vander Waal forces bind the nanotubes in the form of bundles resulting in poor dispersion. To overcome this problem, researchers have used covalent functionalization technique, which directly attaches a functional group to the carbon atoms present on the CNT surface. The attached functional group helps in dispersing CNTs by bonding itself with a variety of organic solvents. This technique, however, involves treatment of nanotubes with strong acids that damages their physical structure to a greater extent [14–16]. It also results in the conversion of most of their sp^2 bonds into sp^3 bonded carbon atoms, reducing the available adsorption sites for VOCs on the CNT surface. We have shown, in our earlier communication [17], that through direct cycloaddtion to π electrons of the CNT, the functionalization can be achieved with reduced damage. This preserves the native structure and properties of the nanotubes leading to enhanced sensing

* Corresponding author. Fax: +91 11 24115270.
E-mail address: aman.arora50@gmail.com (A. Kaur).

http://dx.doi.org/10.1016/j.mssp.2015.08.010
1369-8001/

response. The sensor was fabricated by developing a composite film of functionalized-multiwalled carbon nanotubes (f-MWCNTs) and polymethylmethacrylate (PMMA).

The major factor that greatly influences the response of the sensor is the relative concentration of polymer and nanotubes in the composite. The concentration of polymer governs the spacing among the polymer chains through which the analyte molecules can move towards the CNT surface. The higher will be the concentration of polymer, lesser will be the spacing available for molecules to pass through. In this case, the analyte molecule interacts only with the top layer of polymer chains and is unable to alter the properties of CNTs. The concentration of polymer, therefore, should be optimum to allow passage of VOCs towards nanotubes and to hold the individual nanotubes in the form of an interconnected network. As far as, the concentration of nanotubes in the polymer matrix is concerned, we have already shown that the sensor exhibits excellent performance if the concentration of CNTs is just above the percolation threshold. This is due to the fact that response of the sensor depends on the relative change in resistance of the composite film caused by their swelling due to absorption of VOCs in the polymer matrix. Upon swelling, the gap between the conducting tube increases and thus resistivity of the composite film increases. This increase in resistance can be maximum if concentration of CNTs is just above the percolation threshold value, which will guarantee sufficient conductivity change [12]. A schematic diagram showing the effect of debundling of nanotubes after functionalization and swelling of PMMA molecules is shown in Fig. 1.

In the present work, we have focused on another important characteristic of the composite sensor i.e. selectivity. It is the ability of a sensor to detect a particular vapor in an ambient where other vapors may also be present. This characteristic is jointly governed by the electronic and structural properties of both the species i.e. the sensing material and the vapor molecule. Also, the discrimination towards different organic vapors strongly depends on the adsorption and chemical properties of the analyte. We have analyzed the selective behavior of the PMMA: f-MWCNT composite film by exposing it to 10 different organic vapors namely

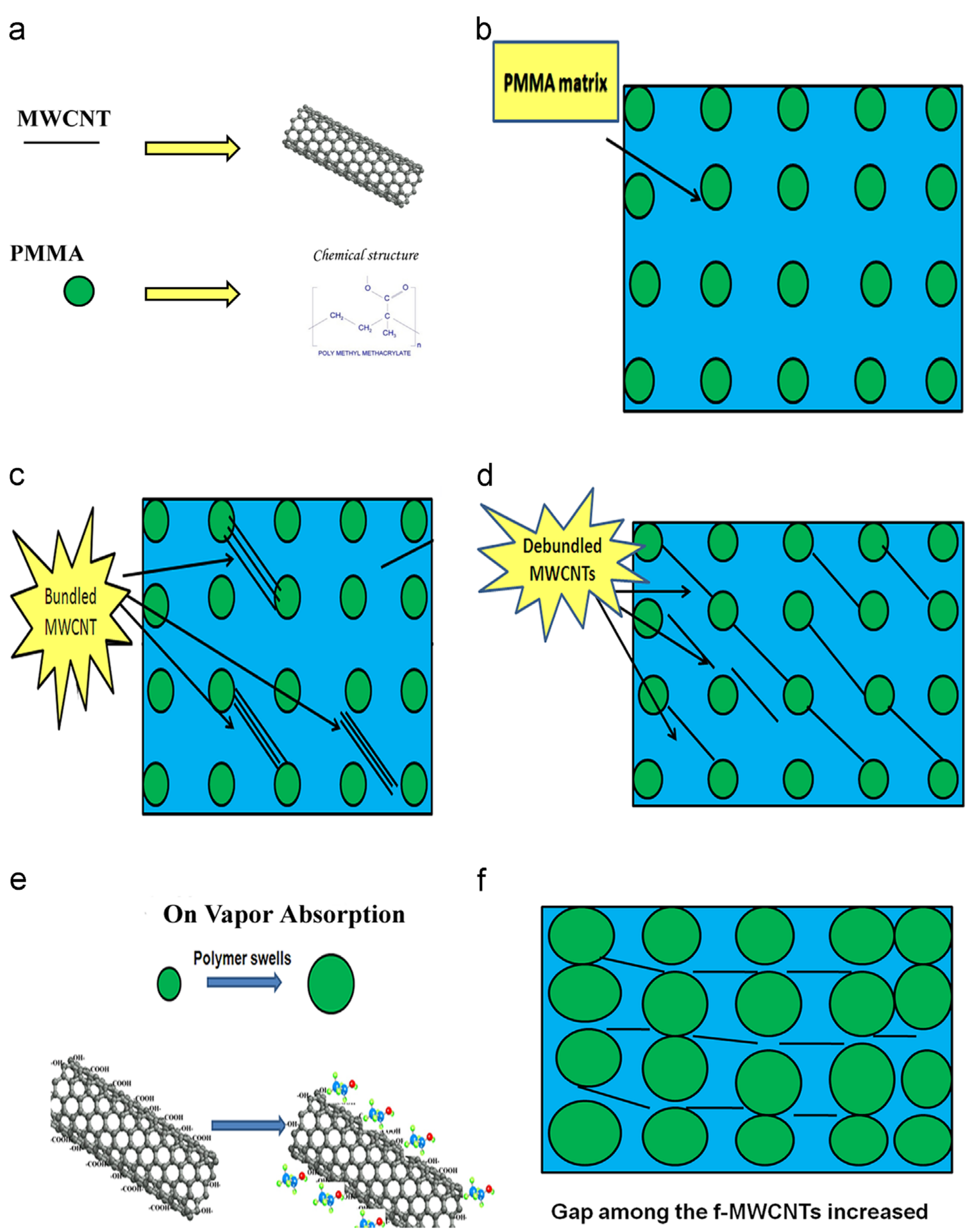

Fig. 1. A schematic diagram showing the effect of debundling of nanotubes after functionalization and swelling of PMMA molecules on exposure to VOCs.