Talanta 107 (2013) 239–247

Contents lists available at SciVerse ScienceDirect

Talanta

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

Flexible sensor based on carbon nanofibers with multifunctional sensing features

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ARTICLE INFO

Article history:
Received 24 May 2012
Received in revised form
4 January 2013
Accepted 11 January 2013
Available online 21 January 2013

Keywords:
Inkjet
Gas sensor
Room temperature
Carbon nanofibers
Flexible electronics
Mutifunctional

ABSTRACT

Herein, we present the fabrication and characterization of a flexible gas sensor based on carbon nanofibers. The sensing device is composed of interdigitated silver electrodes deposited by inkjet printing on Kapton substrates, subsequently coated with carbon nanofibers as sensing element. Gas sensing response to CO, NH_3 and humidity has been characterized in detail. Thermal, mechanical and electromagnetic radiation effects have also been studied and discussed from the point of view of the cross-sensitivity. The obtained results open the door for a new generation of flexible sensors with multifunctional sensing features, which are producible with scalable techniques based on low cost nanomaterials.

1. Introduction

The development of new smart sensor networks for the monitoring of environmental parameters for comfort, health, safety, and security purposes demands for new solid state gas sensors with better performances. Up to now, considerable effort has been devoted to improve operating parameters such as sensitivity, selectivity, and reliability of the sensors.

For on-site monitoring applications, devices with low power consumption, low-cost, high efficiency, and portability are highly desirable. Some demonstrations of such devices are under investigation and involve the development of sensors based on flexible substrates, partially owing to the increasing proliferation of handheld, portable consumer electronics [1,2]. Fabrication of flexible sensor platforms has been investigated and provides a wide range of applications, featuring low cost, light weight and mechanical flexibility [3]. Devices supported on plastic foils are required to realize intelligent RFID tags for environmental monitoring, flexible active matrix displays, electronics skins, flexible solar cells and disposable printed electronics [4–7], and represent a cost effective alternative to expensive silicon technology, which could eventually find application in wearable systems, smart buildings, and in the logistics of perishable products. The pending challenges are not only their manufacture, but also the stability of their mechanical, electrical and gas sensing properties.

Printed electronics are becoming a more and more mature technology every day, and new kinds of products are expected in the near future. Besides, a strong potential for cost-effective production with a reduced infrastructure, the benefits of printing devices on plastic foil include their potential to be lightweight, foldable/rollable, transparent, thin, conformal, wearable, and produced on a large scale. In the last decade, inkjet printing has grown to a major topic in scientific research. Today, inkjet printing is a competitive method to conventional printing techniques such as photolithography for the production of electronic devices [8,9]. Furthermore, inkjet printing is compatible with many types of substrates, non-contact and no-mask patterning, low temperature processing, and no requirement for vacuum [10,11].

There are a limited number of publications on gas sensors on plastic/flexible foils, but this number is growing up. Most of these works used substrates as polyethylene-terephthalate (PET), polyethylene naphthalate (PEN) and polyimide (PI). As a matter of fact, Torsi et al. fabricated a thin-film transistor gas sensor, comprising an outermost layer with built-in enantioselective properties that exhibits a field-effect amplified sensitivity that

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http://dx.doi.org/10.1016/j.talanta.2013.01.022

enables differential detection of optical isomers in the range of tens-of ppm [12]. Other works reported on the detection at room temperature of volatile organic compounds, sub-ppm levels of ammonia and hydrogen sulphide, and ppm levels of nitrogen oxides, some of which using printing technologies (e.g., inkjet printing) to deposit gas-sensitive conducting polymers and silver electrodes [13–18]. However, the sensing performance achieved was poor and requires further development to meet the sensing performances and reliability demanded by the market, as discussed by Subramanian et al. [19].

In the present paper, a new approach for developing flexible gas sensors based on carbon nanofibers is presented. Our aim is to achieve an easy, fast and inexpensive methodology to produce low power consumption gas alarms integrable in textile or other non-usual localizations. For this purpose, Kapton was used as flexible substrate, due to its physical and chemical advantages, on which interdigited silver electrodes were deposited by inkjet printing methods. These were later coated with carbon nanofibers by means of spray technique [20,21]. Carbon materials, which are well-known by rendering significant responses to gases even at room temperature, permit to lower the power consumption of the sensor. In order to evaluate the performance of the sensors developed, their gas sensing properties to CO, NH_3 and humidity at room temperature as well as the effects of thermal, mechanical and electromagnetic radiation stimuli were thoroughly studied.

2. Experimental

2.1. Sensor fabrication

Kapton (polyimide) commercially available from DuPont, with thickness of 50 μm, was chosen as flexible substrate. It has a typical dielectric strength of 240 kV/mm [22], which makes it suitable for electronic circuitry. The key advantages of this polyimide compared to other polymers is that it can be heated up to 350 °C, as a second order glass transition occurs between 360 °C and 410 °C [22]. Therefore, moderate thermal treatments of the materials can be performed even after being deposited. From the mechanical point of view, it also displays good flexibility and resistance [22]. Another advantage, which is common in most of the polymers, is its low mass, which makes it more resistant to vibration and sudden mechanical energy transfers. This makes it appropriate for future devices more reliable in environments, such as automotive applications, where mechanical resistance is a special concern. All these points justify the election of Kapton as flexible substrate used in this present work.

The fabrication of the metal contacts was made by inkjet deposition of commercial silver ink U5603 (SunTronic Inc., USA) with 20 wt% of silver. An automatic controlled inkjet system with inkjet dispenser Xenjet 4000 (Xennia Technology Ltd., UK). The cartridge was an Omnidot 760 (Xaar, Ltd., UK), based on piezo-resistive technology to eject the ink. Once the ink was deposited, the circuits were heated to 200 °C for 20 min to stabilize the silver and evaporate the ink's solvent. Several designs were conceived and implemented: ten conductive bars (with widths of 0.7 mm for each bar and pitch of 1 mm between them designed following the specifications of a commercial FFC/FPC connector), two conductive bars (2 mm wide and pitch of 2.54 mm designed for a clincher commercial socket), 4-probes circuit optimized for van der Pauw measurements [23,24], and interdigited configuration for sensor testing. This last one included several alternative variations: terminations for FFC/FPC connector and square pads for probe station testing. Examples of interdigited printed circuits used in this work are showed in the Supplementary materials.

2.2. Material deposition

Carbon nanofibers, supplied by Grupo Antolín, having a diameter between 20 and 80 nm and lengths of more than 30 μm, were first dispersed in 2-propanol and then deposited over interdigited silver electrodes using spray technique [20,21]. The deposited film was homogenous with a thickness of hundreds of nanometers except for the edges, which displayed a linearly growing profile. Two kinds of nanofibers were tested, one with a graphitization of ~70% (GANF) and one with ~100%, (GANFG), further details of these nanofibers have been given elsewhere [25].

2.3. Characterization

A series of experiments were designed and performed in order to evaluate the electrical, thermal, mechanical and sensing properties of the devices based on GANF and GANFG nanofibers. The response of the sensor to gas and by radiation was defined as the difference between the resistance when there is a change of the physical measured property (R), and the initial resistance value (R_0) normalized to R_0.

$$\text{Response}(\%) = \frac{R - R_0}{R_0} \times 100 = \frac{\Delta R}{R_0} \quad (1)$$

2.3.1. Electrical and thermal characterization

To evaluate the electrical properties of the samples, different kinds of measurement were conducted using a sourcemeter unit SMU 2400 (Kethley Ltd., USA) and a multimeter 3458A (Agilent Inc., USA). All connected to 4-probes station, which featured a temperature controller capable of setting the sample's temperature from room temperature (25 °C) up to 300 °C. Tungsten probe tips (72T-J3 from American Probe & Technologies Inc. USA, with straight shape and radius of 7 μm) were used to obtain a reliable and stable contact with the silver pads of the samples. All the temperature treatments shown below were carried out in ambient atmosphere. First of all, studies of the sheet resistance of the nanofibers were done using the van der Pauw method [23,24]. These resistance values were quite independent of the asymmetry between contacts of the thermoelectric contributions at each different metal-fiber interface.

Subsequently, in order to study the contribution of the contacts interface to the total resistance of the sample, measurements of the resistance of the fibers films at different interelectrode distances were conducted. The total resistance of the sample can be easily rationalized as a contribution from the two contacts and a contribution from the fibers. Therefore, we can write:

$$R_{\text{measured}-2P} \equiv R_{\text{sample}} + 2R_c \quad (2)$$

where $R_{\text{measured}-2p}$ is the experimental value of the total resistance (defined as R_{2P} since it is the resistance measured in 2-probes studies), R_{sample} is the intrinsic resistance value of the nanofibers film, and R_c is the resistance of each one of the contacts between the nanofibers and the silver electrodes. Since the R_{sample} is expected to be proportional to the distance between contacts l, then it is easy to determine R_c by extrapolating the value of the total resistance at distance zero from a series of $R_{\text{measured}-2p}$ values vs. l. The extrapolated point gives a direct measurement of the contribution of the contacts to the total value of measured resistance.

2.3.2. Gas testing

Sensing characterization was carried out in a gas test system conceived to characterize micro and nanodevices, which included a MGP-2 gas mixer (Gometrics S.L., Spain) and a 4200-SCS Semiconductor Characterization System equipped with 3 sourcemeter