Sensors and Actuators B 174 (2012) 577–585

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

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

1/*f* noise and its unusual high-frequency deactivation at high biasing currents in carbon black polymers with residual $1/f^{\gamma}$ ($\gamma = 2.2$) noise and a preliminary estimation of the average trap energy

Christian Falconi[a,b,*], Corrado Di Natale[a,b], Eugenio Martinelli[a], Arnaldo D'Amico[a], Emiliano Zampetti[c], Julian W. Gardner[d], Carolyne M. Van Vliet[e]

[a] Department of Electronics Engineering, University of Rome "Tor Vergata", 00133 Rome, Italy
[b] CNR IDASC, Via Fosso del Cavaliere, 100, 00133 Rome, Italy
[c] CNR IMM – Sezione di Roma, Via Fosso del Cavaliere, 100, 00133 Rome, Italy
[d] Microsensors and Bioelectronics Laboratory, School of Engineering, University of Warwick, Coventry CV4 7AL, UK
[e] Dept of Physics, University of Miami, P.O. Box 248046, Coral Gables, FL 33124, USA

ARTICLE INFO

Article history:
Received 22 October 2011
Received in revised form 30 March 2012
Accepted 23 July 2012
Available online 3 August 2012

Keywords:
Noise
Carbon black polymers
1/*f* noise
Chemical sensors

ABSTRACT

We have performed noise measurements on 5 different carbon black polymer composite resistive gas sensors, both in an inert chemical atmosphere (dry nitrogen) and in an active chemical atmosphere (with toluene or ethanol vapour). All the sensors exhibited the presence of significant 1/*f* noise for biasing currents in the μA range; moreover, we show that the level of 1/*f* noise is strongly dependent upon the chemical environment and, in particular, the concentration of the vapour. These results, obtained for the first time with this chemically sensitive nanocomposite material, should help in the creation of circuit models and also in the design of low noise chemical sensors using carbon-black composite materials. Additionally, in the thinnest sensor, at sufficiently high biasing currents we found the deactivation of 1/*f* noise above a certain frequency, with an unexpected residual $1/f^{\gamma}$ excess noise (γ around 2.2) which, to our knowledge, has not been observed before. Interestingly, this unusual excess noise was almost insensitive to the presence of either toluene or ethanol vapour; this observation may offer insight on the origins of both 1/*f* and the measured $1/f^{\gamma}$ excess noise in composite polymer resistors. Finally, we have estimated the available noise energy per trap for a given adsorption process which may be used to characterize the noise fluctuations in a chemical environment. We believe that our work will also enable the construction of better SPICE models to help in the design of advanced CMOS transduction circuitry.

1. Introduction

Because the ultimate resolution of a sensor (or its electronic interface) [1] is generally determined by noise in the sensing material, it is of fundamental importance. Noise has been studied in materials and electronic devices in the past years [2–8] but less so in the field of gas sensing. Despite impressive efforts at both the experimental and theoretical level, noise phenomena are still the subject of open questions and controversies (e.g. see [5,7,9]), probably due to their complexity and to the multitude of possible mechanisms behind measurable fluctuations. The situation is even more complex in chemical sensors where additional fluctuations can originate from the interaction between the sensing layer and its chemical environment; these additional fluctuations may even dominate the total noise [10].

Beside optimization of resolution of sensors and electronic interfaces, there are other crucial motivations for studying noise. In fact, noise is not always deleterious [10–12] and has, for instance, been correlated with the quality or reliability of devices [11,13], with electro-migration in metal interconnects [14], with the quality of electro-chromic devices (i.e. devices whose optical transmittance depends on an applied voltage) [15]. As additional examples, noise in electrochemical cell-substrate impedance sensing (ECIS) systems has enabled the detection of cancerous cells [16] and toxin levels [17]. Especially relevant for this paper, it has been first shown in [10] that noise can also provide information for the detection of volatile chemicals; this result is however not general; for instance, with reference to carbon-black polymer composite resistive chemical sensors, in [18] both resistance and noise power

* Corresponding author at: Department of Electronics Engineering, University of Rome "Tor Vergata", 00133 Rome, Italy.
E-mail address: falconi@eln.uniroma2.it (C. Falconi).

0925-4005/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.snb.2012.07.095

spectra variations due to methanol, propanol, and hexanol were measured and it was concluded that the combination of resistance and noise measurements did not give more information than resistance measurements alone.

In this paper we focus on a certain type of composite polymer resistive chemical sensor. In general, the resistivity of composites consisting of conductive particles in an electrically insulating matrix strongly depends on the concentration c of the conductive particles and, very interesting for sensing applications, may change by orders of magnitude for small variations of c; though more complex models (e.g. [19]) may be necessary, this high sensitivity may be qualitatively explained by the classical percolation theory (e.g. see [20]). In practice, at very low values of c, the resistivity is very high and approaches the resistivity of the insulating polymer; when c is gradually increased the resistivity slowly decreases until the first "continuous or percolation path" of conductive particles is formed (called the percolation threshold); further increases of c will result in very sharp reductions of the resistivity until the composite resistivity approaches the resistivity of the conductive particles (conduction limit) so that further increases of c do not significantly change the resistivity. These high sensitivities can be advantageously used for thermistors, pressure sensors, mechanical sensing [21] and chemical sensors [20,22,23]. In particular, after in [20] it was reported that the resistivity of carbon black polymer composite films could change by orders of magnitude when exposed to certain volatile organic compounds, chemical sensors of this type have been widely used (including in the Cyranose commercial handheld electronic nose[1]). Clearly, besides high sensitivity, low noise is also crucial for good resolution; this is a first important practical reason for characterizing carbon black polymer composites from the point of view of their intrinsic fluctuations. Additionally, similar to [10,12], even in this type of sensor noise could also contain useful information; though this was not the case in the carbon-black composite described by [18], it is typically difficult to derive general conclusions on similar composites due to the complexity of predicting the effects of differences in carbon-black and/or in the matrix [24]. Another motivation of this work is to compare noise measurements on our sensors with available models and experimental data concerning the noise measured on other thick film resistors [18,24–39] and also with noise of conductive nanostructures in insulating polymer [40]; in fact, besides providing data for the theory of fluctuations, noise measurements can also play a key role in the validation of models for electrical transport (e.g. see the validation of the percolation-tunneling model in carbon black composites [19,37]).

In all our 5 gas sensors we found large $1/f$ noise that was sensitive to both ethanol and toluene concentration levels and also contained additional information when compared to the standard resistance measurement (similar to [10] and different from [18]). Moreover, we found, in only one of our sensors, at sufficiently high biasing currents (i.e. there is a biasing current threshold), the deactivation of $1/f$ noise above a certain frequency with an unexpected residual $1/f^{\gamma}$ excess noise (γ around 2.2). In striking contrast with the normal $1/f$ noise, this residual noise was nearly insensitive to both ethanol and toluene; as another distinct characteristic, different from $1/f$ noise, the existence of a current threshold unambiguously demonstrates that our $1/f^{\gamma}$ excess noise is not related to pure resistance fluctuations. As we shall discuss later, to the best of our knowledge, in previous papers on noise of thick film resistors the values of γ were always smaller than 1.5 [18,24–27,29,31–33] and there are no models or data on noise of thick film resistors which are consistent with our noise measurements.

The paper is organized as follows: in Section 2 we describe our sensors that use poly(styrene-co-butadiene) AB block copolymer with 30% of styrene, a material currently employed for the detection of volatile compounds in electronic nose development; five resistive sensors having different average thicknesses (see Table 1) have been deposited by air spraying onto a microfabricated device with a resistive microheater. In Section 3 we present our experimental method; Section 4 presents our measurements and relative discussions. Finally, conclusions are drawn in Section 5.

2. Sensors description

The resistive sensor (SRL127) was designed by the Sensors Research Laboratory[2] at Warwick University for the characterisation of polymer or metal oxide based gas-sensitive films. The SRL127 device has been fabricated by standard silicon processing techniques: 200 nm of silicon nitride have been deposited by LPCVD on a silicon wafer with oxide passivation; afterwards, 10 nm of chrome and 250 nm of gold have been deposited (chrome is used as an adhesion promoter). Photoresist was spun down and the gold patterned using standard UV lithography. Finally a photoresist layer was deposited and soft baked to form a passivation layer over the device; this passivation layer was patterned before baking using photolithography, thus opening up the sensing area and bond pads with the final device about 4 mm × 4 mm in size. The device contains both the gold co-planar sensing electrodes and a lateral resistive heater. The sensing electrodes were separated by a gap of 50 μm and open length of 1000 μm on top of which the active composite material was spray coated. The heating element surrounded this central sensing structure and can be used to increase the temperature of the active film. To reduce the power consumption of the heater the silicon substrate has been anisotropically back-etched with the oxide acting as an etch stop to create a thin thermally-isolated membrane under the sensing and heating elements. Fig. 1 shows a schematic cross section of a sensor and a photograph of the fabricated device.

We have used different samples in order to investigate the role of the average thickness on both the variations of resistance and excess noise upon exposure to variations of the chemical environment.

The polymer used in the composite films for these experiments was one commonly used in previous work, namely poly(styrene-co-butadiene) AB block copolymer with 30% of styrene. The deposition of the polymers was carried out at Warwick University using recipes provided by Cyrano Sciences Inc., USA. The polymer was dissolved in toluene at a 0.625% loading by weight of total solids to toluene and stirred continuously for a minimum of 24 h. The polymer carbon black nanospheres (Black Pearls 2000, Cabot, USA)/toluene was mixed with a 0.375% loading of carbon black and 0.25% polymer and stirred for 30 min before deposition. The deposition was carried out using a BioDot XYZ Platform (BIODOT, Irvine, CA). This combines motion control with an AirJet 2000TM dispenser. This technique produced a circular coating typically 1 mm to 1.5 mm in diameter, over the centre of the device. Different average thicknesses have therefore been easily obtained by choosing different numbers of passes in the deposition, as follows: 9 passes for the devices D and E; 6 passes for the devices B and C; 4 passes for the device A and for another device which showed an open-circuit behaviour (i.e. 4 was the minimum number of passes which allowed to obtain, and not always, functional devices).

Fig. 2 shows an atomic force microscope (AFM) image of these composite materials (Q-Scope™ 788, Quesant Instrument Corp.,

[1] Originally Cyrano Sciences Inc., USA and then Smith Detection Pasadena, USA.

[2] Now called Microsensors and Bioelectronics Laboratory.