



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

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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^γ 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^γ 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.

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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

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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 nose¹). 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 Laboratory² 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 μ m and open length of 1000 μ m 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 Cyranose 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 Cyranose Sciences Inc., USA and then Smith Detection Pasadena, USA.

² Now called Microsensors and Bioelectronics Laboratory.

Table 1
Characteristics of the sensing layers on the gas sensors.

Average thickness (μm)	Diameter of polymer spots (μm)	Volume of the sensor (10^{-3} mm^3)	Initial resistance (Ω)
0.70	1300	0.929	36 k Ω
2.16	1228	2.56	1.94 k Ω
2.29	1234	2.74	1.6 k Ω
1.40	1280	1.8	2.4 k Ω
1.70	1220	1.99	2.65 k Ω

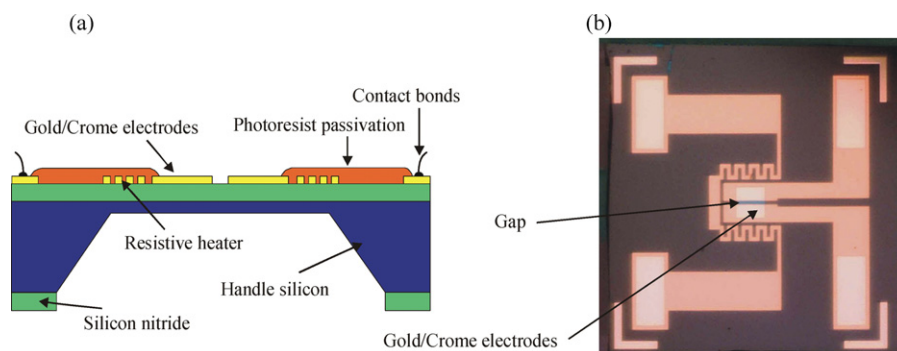


Fig. 1. (a) Schematic cross-section of sensing device and (b) photograph of SRL127 device (uncoated) showing electrodes and meandering heater. Lighter areas are open pads.

USA), thus revealing a typical sphere diameter of around 100 nm, with multi-contacts between carbon spheres.

After polymer deposition the resistive structure was mounted and ultrasonically wire-bonded onto a 14-pin DIL package (Spectrum Semiconductors, USA, part no. CSB1410B).

3. Experimental set up

All the measurements have been performed in a metallic test chamber for shielding environmental interferences and allowing a controlled gas flow.

The current source for biasing the sensors was obtained by using a Thevenin generator (high quality battery with a low noise wire resistors, R_p , in series) with R_p much higher than the sensor resistance (so that the current through the resistance is approximately equal to the battery voltage divided by R_p). The preamplifier, model 5113 (EG&G-PAR), was used in the flat band mode up to 300 kHz; the output of the preamplifier was sent to a spectrum dynamic analyser (HP 35605A) and each measurement was obtained by

considering 200 averages. The total available bandwidth (about 100 kHz) was divided in 4 sub-bands in order to increase the data points in the bandwidth of interest; a satisfactory stitching of the four spectra was obtained, enabling us to estimate the slopes of the curves with better precision.

For each of the five sensors the spectra of the thermal noise voltage and of the excess noise voltage were measured in nitrogen atmosphere and in presence of the toluene and ethanol vapours in dry nitrogen. Measurements were performed at room temperature and in a low flow condition (2 cc/min) and, for validation, also in a static nitrogen atmosphere in order to make sure that the unusual noise behaviour discussed below is not a consequence of turbulence phenomena inside the test chamber.

We stress that all the measurements (i.e. both resistance and excess noise measurements) have been performed after allowing sufficient time so that any transient was completed.

4. Measurements and discussion

The measured geometrical features of the different sensors and the resistance (at room temperature and in dry nitrogen) are given in Table 1; evidently, the measured values of resistances are not inversely proportional to the average thicknesses. This result is,

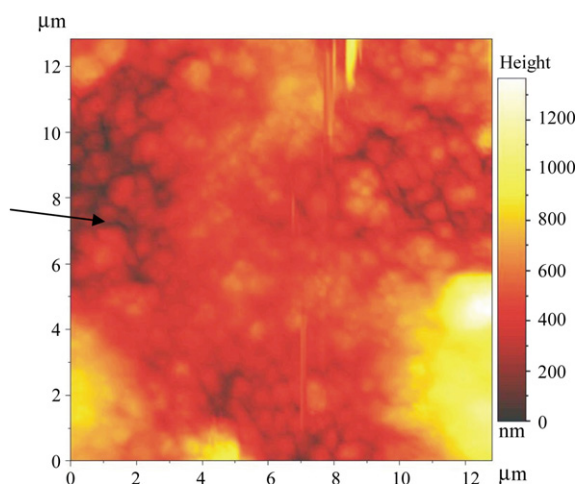


Fig. 2. AFM plot of the composite polymer material with conducting nanospheres apparent.

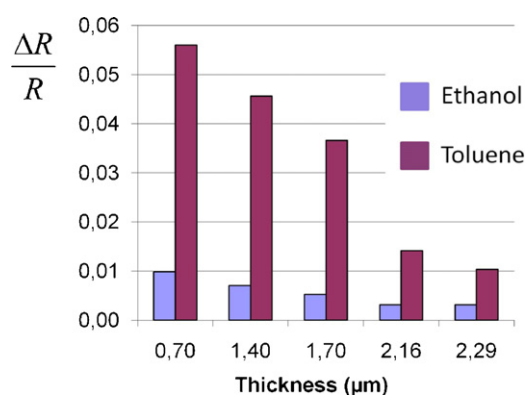


Fig. 3. Relative variations of the resistance $\Delta R/R$.

however, not unexpected: the resistors are likely to be highly inhomogeneous (see Fig. 2), with special reference to thickness (measured thicknesses in Table 1 are average values); significant spread of local resistivity is also expected; the diameters of the spheres which constitute the material are around 100 nm; the electrodes lie below the sensing film and have a thickness of around 260 nm, i.e. comparable with sphere diameters; local work-function variations may induce space charge regions.

Fig. 3 shows the relative variations of the resistances of the five sensors when exposed to 60,000 ppm of ethanol (80% of saturation

vapour pressure) and to 22,200 ppm of toluene (60% of saturation vapour pressure) in nitrogen, respectively; as expected, the relative variation of the resistance is higher for sensors with smaller average thickness (the effect of surface variations will obviously be stronger for smaller thicknesses).

Fig. 4 shows, for all the 5 sensors, both in presence and in absence of the ethanol vapour, the noise voltage spectral densities measured without biasing current (Johnson noise and background noise) and with a biasing current equal to $10\mu\text{A}$ for the sensor A and to $110\mu\text{A}$ for all the other sensors. Taking into account the initial resistances

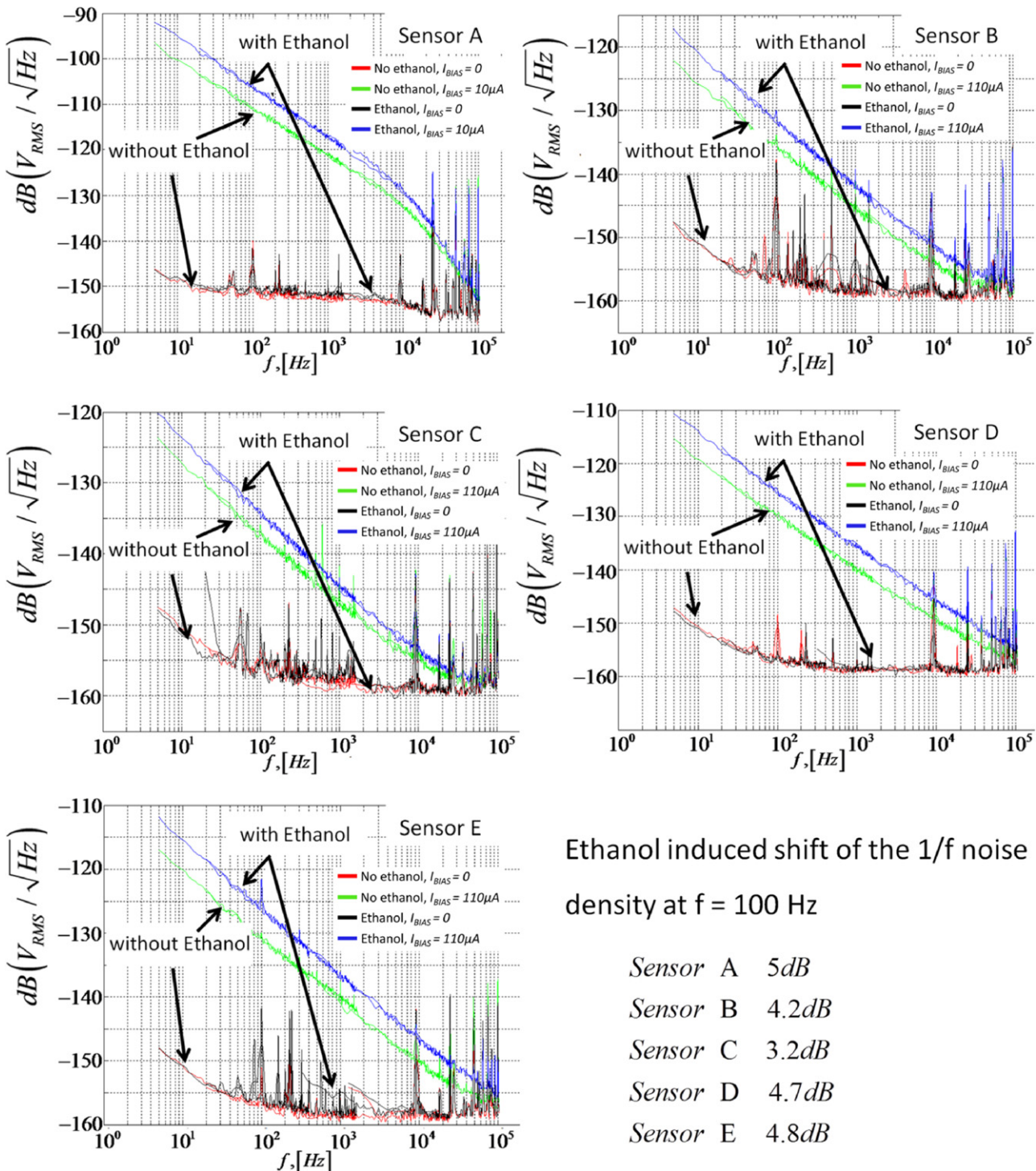


Fig. 4. Noise measurements for the sensors A, B, C, D, and E; for each sensor the noise voltage spectral density is shown both with and without biasing current, both in presence and in absence of ethanol.

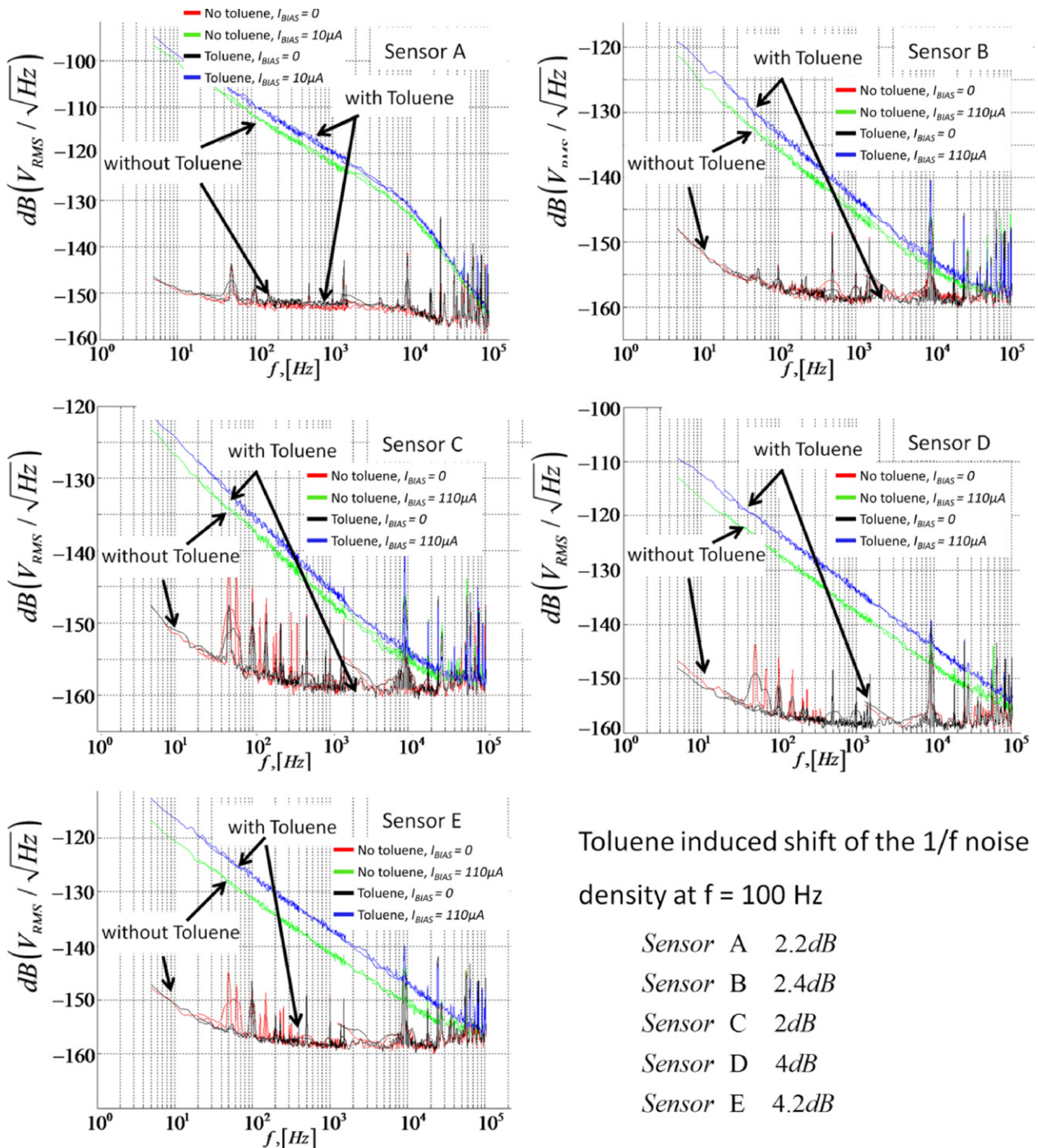


Fig. 5. Noise measurements for the sensors A, B, C, D, and E; for each sensor the noise voltage spectral density is shown both with and without biasing current, both in presence and in absence of toluene.

(Table 1), the values of the biasing currents are such that all the sensors have similar biasing voltages (i.e. similar electric fields because the electrodes are nominally identical).

Fig. 5 shows, for all the 5 sensors, the noise voltage spectral density measured without current (Johnson noise and background noise) and with a biasing current, both in presence and in absence of the toluene vapour. Similar to previous measurements, the biasing current was $10 \mu A$ for the sensor A and $110 \mu A$ for all the other sensors.

By comparing noise and resistance measurements, we find that the relative variations of the noise voltage spectral density are, for the same concentrations of volatile compounds and for a given sensor, much larger. As an example, for the thinnest sensor, the noise voltage spectral density is increased up to 5 dB in presence of ethanol, which corresponds to about 1.78 increase of the noise voltage spectral density, which is much larger than the correspondent relative resistance variation (below 6%). This larger relative variation of the noise spectral densities may be justified as follows.

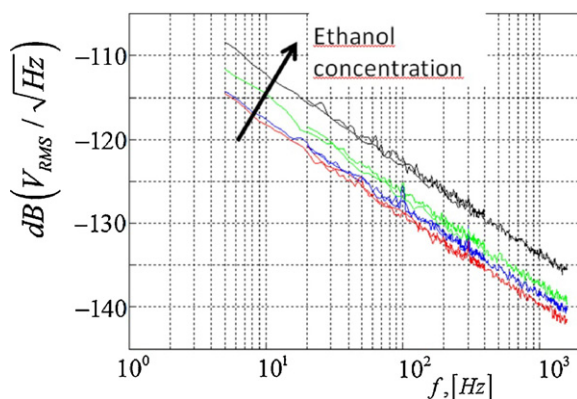


Fig. 6. $1/f$ noise voltage spectral density at different concentration of ethanol.

If, as a very crude approximation, we assume that each adsorbed molecule induces one additional trap (which will result in additional fluctuations) and one additional carrier, since the number of carriers is much larger than the number of traps, the relative variation of resistance is expected to be much smaller than the relative variation of the excess noise.

Furthermore, Figs. 4 and 5 show that noise is more sensitive to ethanol than to toluene vapour; on the contrary, Fig. 3 shows that DC relative resistance variations are higher in presence of toluene with respect to ethanol; this simple consideration suggests us that the combination of noise (trap states) and resistance measurements (swelling) offer more information than the resistance measurement alone. In fact, for instance, if only ethanol and toluene are present in the chemical environment, a single sensor could discriminate between ethanol and toluene by combining resistance and noise measurements (e.g. in contrast to ethanol, toluene would result in a relatively high resistance variation and in a relatively small noise variation). This result, similar to [10], is different from [18] which was also obtained with carbon-black polymer composites; similar differences confirm that it is extremely difficult to derive general conclusions on carbon-black composites due to significant effects of even small differences in carbon-black and/or in the matrix [24].

Interestingly, although a detailed analysis of the interactions of toluene (aromatic water-insoluble hydrocarbon) and ethanol (2-carbon alcohol) with the sensor is beyond the scope of this paper, we observe that since toluene is a solvent for the polymer, the partition coefficient for toluene is expected to be larger than for ethanol, consistent with the observed resistance changes (Fig. 3, with the ethanol concentration about three times larger than toluene concentration). Moreover it is unlikely that toluene and ethanol will be in competition within the film as they are hydrophobic and hydrophilic—so they should be linearly separable. The ethanol could compete with water molecules in its partitioning but here we are making measurements in dry nitrogen. The different behaviour of excess noise may probably be attributed to the very different electric dipoles (1.7 Debye) of ethanol and (only 0.4 Debye) of toluene; the higher electric dipoles of ethanol molecules are likely to have a stronger influence on the adjacent charges, possibly resulting in a larger increase of fluctuations.

As an illustrative case, Fig. 6 shows $1/f$ noise voltage spectral densities for the sensor D, at 0, 15,000 ppm, 30,000 ppm, and 60,000 ppm of ethanol in dry nitrogen (higher concentrations result in higher noise).

Fig. 7 shows the noise voltage spectral density for sensor A at different biasing currents. From this figure we observe that for very low currents (below about $1 \mu\text{A}$) the measured excess noise is of $1/f$ type; for larger currents the $1/f$ behaviour is deactivated above a certain frequency and only a noise spectrum whose slope is about

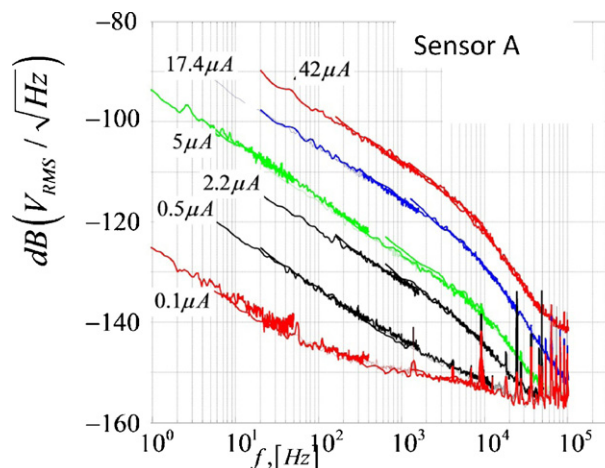


Fig. 7. Noise voltage spectral density of the sensor A in nitrogen with different biasing currents.

–22 dB/decade is left; for simplicity we will refer to this as the $1/f^\gamma$ noise (γ is about 2.2). Several considerations demonstrate that our unusual $1/f^\gamma$ noise concerned only the thinnest sensor (which is also the sensor having the highest resistance, about $36 \text{ k}\Omega$ in nitrogen), is not originated by a parasitic filter or other artefacts: first, the expected cut-off frequency of the low pass parasitic filter associated with the sensor is, at least, ten times higher than the “breaking frequency” where the $1/f^\gamma$ noise appears; second, the slope of a $1/f$ noise filtered by a first order low pass filter would be –30 dB/decade; third, the measurements with different chemical environments demonstrate that there is no filtering of the noise (in fact an hypothetical filter would filter in the same way the $1/f$ noise, independently on the chemical environment, so that the distance (in dB) between the noise voltage spectral densities obtained in different chemical environments should not vary with frequency). The time constant associated to the transition between $1/f$ and $1/f^\gamma$ noise is around $150 \mu\text{s}$ (much faster than the time constant of the sensor response, in the order of 100 s).

In our measurements, distinct from $1/f$ noise, there is a threshold current and the fluctuations are clearly not just conductance fluctuations (otherwise the distance, in dB, between two curves correspondent to two different current levels would be constant and not change with frequency). Though it is well known that some types of fluctuations strongly depend upon the biasing currents, previously reported noise measurements and models are not consistent with our results. For instance, in [28] the noise (measured at a fixed frequency equal to 0.5 Hz) was anyway $1/f$ noise and, very important, increased at high current densities; in our sensor, at high current densities, the $1/f$ noise is deactivated above a certain frequency and only a $1/f^\gamma$ excess noise is left (thus, first, noise is decreased and, second, our noise is not simply $1/f$ noise). Additionally, though the value of γ is around 2.2, our noise is also distinct from the “so-called $1/f^2$ noise” [11] whose voltage noise spectrum can be empirically described by

$$S_v(f) = \frac{I^\beta C}{f^\gamma T} \exp\left(\frac{-E_a}{kT}\right) \quad (1)$$

where C is a parameter depending on technology and geometry of the device, $\beta \geq 3$ (values from 3 to 7 have been reported according to [41]), $\gamma \geq 2$, I is the DC biasing current, T is the absolute temperature, k is the Boltzmann constant, and E_a is the “electromigration activation energy from noise measurements” [11]. In fact, this class of fluctuations (which must be attributed [11] to the DC-current induced electro-migration, resistance drift and resistance fluctuations) is found in metal resistors with extremely high current

densities (typically leading to electromigration) which are orders of magnitude higher than in our experiments; moreover, in our samples (conductive particles embedded in insulating polymers), distinct from homogeneous resistors, the fluctuation genesis is likely related to tunnelling between adjacent particles; finally, the empirical model (1) does not fit our measurements; for instance, the ratio between the biasing currents 42 μA and 17.4 μA is about 2.41 which would correspond, for a value of β larger than 3 (as predicted by (1)), to an increase of at least 14 times in the noise spectral power density, which is clearly much more than the measured noise increase.

Very importantly, in striking contrast with the $1/f$ noise, by inspection of Figs. 4 and 5, we see that in both cases the chemical interaction with the environment only slightly modifies the $1/f^\gamma$ behaviour; though the identification of a noise model is beyond the scope of this paper, we believe this observation may offer insight on the origin of both our $1/f$ and $1/f^\gamma$ excess noise.

We also point out that above a certain current density (the transition from $1/f$ to the unusual $1/f^\gamma$ behaviour only happened in sensor A) some mechanisms for $1/f$ noise may be deactivated above a certain frequency. It is also useful to remind that, for instance, the McWerther model allows to find a white noise at very low frequencies, a $1/f$ noise in the intermediate frequency range, and a $1/f^2$ noise in the high frequency range; however, beside the difference between 2 and 2.2, our measurements are not consistent with simple conductance fluctuations (otherwise, first, there would not be a threshold current and, second, the distance, in dB, between two noise voltage spectral densities correspondent to two different biasing currents would be constant over frequency).

After the adsorption process has been completed (stationary conditions), it is possible to compute, for a given bandwidth B , the total available (i.e. with a matched load) power of the additional, chemically induced fluctuations, which is the difference ΔP_{av} between the final available noise power $P_{fin,av}$ and the initial available noise power $P_{in,av}$

$$\begin{aligned} P_{in,av} &= \frac{1}{4R_{in}} \int_B S_{in}(f) df \\ P_{fin,av} &= \frac{1}{4R_{fin}} \int_B S_{fin}(f) df \\ \Delta P_{av} &= P_{fin,av} - P_{in,av} = \int_B \left[\frac{S_{fin}(f)}{4R_{fin}} - \frac{S_{in}(f)}{4R_{in}} \right] df \end{aligned} \quad (2)$$

Moreover, assuming the chemically induced noise is originated by traps, it is also possible to estimate the available (i.e. with a matched load) energy involved in such interactions. In fact, if we assume that the entire adsorption–desorption process is a succession of reversible processes and that, upon exposure to a given gas, the noise spectral density time evolution in presence of gas qualitatively follows the resistance response with the same time-constant τ , we can write (for simplicity we consider the initial time of the adsorption process equal to zero, $t_{in} = 0$)

$$\begin{aligned} R_{final} &= R_{in} + (R_{final} - R_{in})(1 - e^{-t/\tau}) \\ S_{final} &= S_{in} + (S_{final} - S_{in})(1 - e^{-t/\tau}) \end{aligned} \quad (3)$$

Within such model, since in our measurements we found noise variations much larger than resistance variations (see above discussions) we may, as a rudimentary approximation, consider an average value for the resistance in the expression for the available power as a function of time,

$$P_{av}(t) = \frac{1}{4R(t)} \int_B S(f, t) df \simeq \frac{1}{4R_{AVG}} \int_B S(f, t) df \quad (4)$$

so that we can compute the total noise available energy in the bandwidth B and in a given time interval from 0 to t_{fin} by integrating the

noise available power as follows

$$\begin{aligned} E_{av} &\simeq \frac{1}{4R_{AVG}} \int_0^{t_{fin}} \left\{ \int_{f_1}^{f_2} [S_{in} + (S_{fin} - S_{in})(1 - e^{-t/\tau})] df \right\} \\ &\times dt = \frac{1}{4R_{AVG}} \int_0^{t_{fin}} \left\{ \int_{f_1}^{f_2} [k_{in} + (k_{fin} - k_{in})(1 - e^{-t/\tau})] \frac{1}{f} df \right\} \\ &\times dt = \frac{1}{4R_{AVG}} \int_0^{t_{fin}} [k_{in} + (k_{fin} - k_{in})(1 - e^{-t/\tau})] \ln \left(\frac{f_2}{f_1} \right) \\ &\times dt = \frac{1}{4R_{AVG}} \ln \left(\frac{f_2}{f_1} \right) [k_{in}t + (k_{fin} - k_{in})t + (k_{fin} - k_{in})\tau e^{-t/\tau}]_0^{t_{fin}} \\ &= \frac{1}{4R_{AVG}} \ln \left(\frac{f_2}{f_1} \right) [k_{fin}t + (k_{fin} - k_{in})\tau e^{-t/\tau}]_0^{t_{fin}} \\ &= \frac{1}{4R_{AVG}} \ln \left(\frac{f_2}{f_1} \right) [k_{fin}t_{fin} + (k_{fin} - k_{in})\tau(e^{-t_{fin}/\tau} - 1)] \end{aligned} \quad (5)$$

From the measurements on the thinnest sensor in presence of ethanol (see Fig. 4) we may consider

$$10 \log(k_{in,ethanol}) = -88 \text{ dB} \quad (6)$$

$$10 \log(k_{fin,ethanol}) = -83 \text{ dB}$$

so that

$$\begin{aligned} k_{in,ethanol} &= 10^{-8.8} (\text{V}^2) \\ k_{fin,ethanol} &= 10^{-8.3} (\text{V}^2) \end{aligned} \quad (7)$$

As a result, considering an approximate time constant of 100 s (measured by observing the time variations of the resistances during the adsorption process, see (3)), in the bandwidth ranging from $1/4\tau$ up to 8 KHz, in the time interval from 0 to 4τ (which is required to approximately reach the adsorption equilibrium condition), and an average value of the resistance equal to 36 k Ω , we find that the noise available energy $E_{av,ethanol}$ is

$$\begin{aligned} E_{av,ethanol} &\simeq \frac{1}{4R_{AVG}} \ln \left(\frac{f_2}{f_1} \right) [k_{fin,ethanol}t_{fin} \\ &+ (k_{fin,ethanol} - k_{in,ethanol})\tau(e^{-t_{fin}/\tau} - 1)] \simeq 170 \text{ pJ} \end{aligned} \quad (8)$$

Even if it is difficult to accurately evaluate the number of traps at the surface and underneath the surface, the above calculations may be utilized for a preliminary estimation of the energy per trap. If we consider (10^{12} – 10^{14}) traps per square centimetre and the area comprised between the electrodes (gap equal to 50 μm , length 1 mm), we may estimate that the number of traps is in the range $5 \times (10^8$ – $10^{10})$, so that the available noise energy per trap for ethanol adsorption (with the above mentioned conditions) may be estimated in the range

$$E_{av,trap,ethanol} \simeq 3.5 \times (10^{-19}$$
– $10^{-21}) \text{ J} \simeq (2.2$ – $0.022) \text{ eV} \quad (9)$

Similarly, using the same procedure, the available noise energy per trap in the case of toluene adsorption may be estimated in the range

$$E_{av,trap,toluene} \simeq 1.2 \times (10^{-19}$$
– $10^{-21}) \text{ J} \simeq (0.75$ – $0.0075) \text{ eV} \quad (10)$

Though our calculations involve very crude approximations, this method, combined with a more accurate estimations of the trap density (which is beyond the scope of this paper) may provide insight for understanding noise phenomena originated by interactions with different chemicals and also synthetically characterize noise phenomena associated with a given absorption process.

5. Conclusions

In this paper we have shown a set of noise measurements performed on five resistive sensors based on the non-conducting polymer poly(styrene-co-butadiene) and conducting carbon black nanoparticles. The average thicknesses of the five sensors ranged from 0.7 μm to 2.9 μm . All these samples, analyzed at room temperature in a test chamber filled by nitrogen atmosphere have shown $1/f^\gamma$ noise with γ very close to 1, even with biasing currents below 1 μA . This (with very good approximation) $1/f$ noise was strongly sensitive to the chemical environment and, in particular, was largely increased by exposure to the ethanol or toluene vapour; moreover, we have verified that for our sensors the combination of noise analysis and of resistance measurements can give more information than resistance measurement alone (different from [18] and consistent with [10]), thus confirming that noise could be used as the sensing signal, with the advantage that it is more stable than the baseline resistance and may require a very low bias voltage, especially important for low power, low cost CMOS gas sensors. Our results, obtained for the first time with this material, provide guidelines for the design of low noise chemoresistors using carbon-black conductive particles and more realistic SPICE models for circuit simulations.

Moreover, in one of these samples, the thinnest one, at sufficiently high biasing currents, we found a deactivation of $1/f$ noise above a certain frequency with an unusual residual $1/f^\gamma$ noise spectral density (γ close to 2.2); this noise, to our knowledge, has never been reported before (e.g. see [18,24–39,42]). In striking contrast with the $1/f$ noise, this residual excess noise was almost insensitive to both toluene and ethanol (even at very high concentrations). The time constant corresponding to the transition between the $1/f$ and the $1/f^\gamma$ noise is around 150 μs , which is much faster than the time response of the sensor. Our results may help understanding the mechanisms of both $1/f$ and $1/f^\gamma$ noise as well as transport phenomena in composite polymer resistors, which are widely used for both physical and gas sensors.

Finally, we have shown a procedure for estimating the available noise energy per trap involved in a given adsorption–desorption process; as an example, we have estimated for the thinnest sensor the order of magnitude of the available energy-per-trap in the case of ethanol and toluene adsorption. The origin of this kind of fluctuations (which would deserve an *ad hoc* investigation due to its complexity) may be related to internal charge transport mechanisms and may concern the superimposition of numerous effects taking place during the adsorption–desorption processes, including hopping, tunnelling, and swelling. We believe that our results will help in the design of more advanced sensor models (including the high noise levels) for use in developing better CMOS interface circuits [43] for a new generation of integrated gas sensors that can be connected wirelessly to the cloud.

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