MWCNT Devices Fabricated by Dielectrophoresis: Study of Their Electrical Behavior Related to Deposited Nanotube Amount for Gas Sensing Applications

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ABSTRACT

Intensive research has been focused on investigating new sensing materials, such as carbon nanotubes (CNT) because of their promising characteristics. However, there are challenges related to their application in commercial devices such as sensitivity, compatibility, and complexity of miniaturization, among others. We report the study of the electrical behavior of devices composed by multi-walled carbon nanotubes (MWCNT) deposited between aluminum electrodes on glass substrates by means of dielectrophoresis (DEP), which is a simple and cost-effective method. The devices were fabricated by varying the DEP process time. Remarkable changes in their electric resistance were noticed depending on the MWCNT quantities deposited. Other electrical properties of devices such as high sensitivity, fast response time and stability are also characterized in humid environment. A humidity sensing mechanism is proposed on the basis of charge transfer between adsorbed water molecules and the MWNTC surface or between water and the glass surface.

Index Terms: Carbon Nanotubes; Dielectrophoretic Deposition, Gas Sensors.

I. INTRODUCTION

During the last few years, fundamental and applied research has been intensified to understand many aspects regarding nanomaterials. Theoretical models have been proposed to describe their special electronic, physical and chemical properties [1, 2], while research in technological area has focused on improving the processes for obtaining these materials in a controlled manner to develop new devices for different applications. In search of effective solutions, several works have documented interesting results related to the development of new sensors based on nanomaterials [3, 4].

In this context, carbon nanotubes (CNT) are interesting alternatives for sensing applications due to their remarkable characteristics, such as high specific area, good electric conductivity, and high mechanical and chemical stability [5-7]. CNT can be divided essentially into two categories: single-walled (SWCNT) and multi-walled (MWCNT) carbon nanotubes. Although SWCNT present advantageous characteristics due to their purity, experimentally MWCNT have been preferred because they can be obtained in large industrial scale, reducing the production cost in comparison to SWCNT.

A critical step to use CNT in sensors is to control their deposition on the surface of devices, and various methods have been developed for this purpose [8-11]. In particular, dielectrophoresis (DEP) is a simple, versatile and cost-effective method to deposit and to align CNT on prefabricated electrodes. This method does not require post processing, and is compatible with existing microfabrication capabilities because it can be conducted at room temperature, in noncorrosive solutions, and with low applied voltage. In DEP processes, the dielectrophoretic force (F_{DEP}) arises when electrodes immersed in a solution (in our case MWCNT solution) are biased by an external non-uniform electric field, inducing dipole moment in the particles. These polarized particles will suffer the action of the F_{DEP}, promoting their motion toward regions of higher electric field gradient, aligning them in parallel with the electric field lines. The DEP method can be optimized to obtain aligned or concentrated MWCNT deposition by adjusting several process parameters such as amplitude, frequency and length of time of the external applied voltage, besides MWCNT morphology, electrode geometries, and solution properties [12].

Recently systematic studies have been conducted to establish better conditions to deposit MWCNT between electrodes by DEP [13]. The potential appli-

cation of the resistive devices fabricated by this technique has also been reported for gas sensing, due to their capability to change electrical characteristics in contact with low concentration gases at room temperature [14, 15]. However, there is a lack of works relating CNT deposition parameters by DEP with the electrical performance of the fabricated devices under different environments.

For this reason, we investigate the electrical behavior of MWCNT resistive devices to establish the relationship between the amount of CNT deposited and their sensitivity to humidity detection towards the development of integrated gas sensors. We propose to use the DEP process to control the CNT localized deposition between interdigitated electrodes with appropriate geometry. The fabricated devices were then submitted to dry N_2 and N_2 saturated with H_20 vapor environments at room temperature to evaluate their response to humidity. Based on the results, electrical conduction mechanisms of fabricated devices were proposed, and a remarkable potential for humidity sensing applications could be verified.

II. EXPERIMENTAL PROCEDURE

A. Devices Fabrication

The fabricated devices are based on interdigitated electrode geometries with locally deposited carbon nanotubes between them by DEP process. Interdigitated electrodes are commonly used for electrical conductivity characterization of nanometer size structures [16]. Our devices are composed of two interdigitated aluminum electrodes with nine fingers each deposited by sputtering over a planar glass substrate. As seen in the inset of Fig. 1, the electrode fingers are composed of triangular geometries to concentrate the electric field during the DEP process and, consequently, to obtain CNT "bridges" or "chains" deposited between them. The minimum separation distance between electrodes is around 5 μm.

The nanotubes used in this work were CVD-grown MWCNT (catalog n. PD15L520, from Nanolab Inc, USA), which were functionalized according to the protocols described in [17]. The DEP MWCNT deposition was carried out with the setup illustrated in Fig. 2, as follows: the MWCNT solution was dropped directly onto the sample, and a sinusoidal signal with $V = 10\ V_{pp}$ and $f = 2\ MHz$ was applied in the circuit by a function generator. A 1 $k\Omega$ shunt resistor was included to allow monitoring the DEP current and to protect the generator in case of short circuit in the electrochemical cell. The oscilloscope was used to measure the applied voltage and the current during this process.

Five different DEP time intervals were applied to fabricate the CNT devices: 2 minutes (device E2), 4 minutes (device E4), 10 minutes (device E10), 30 minutes (device E30), and 60 minutes (device E60). A sample without CNT (device E0) was adopted as reference. After the deposition processes, the samples were rinsed in ethanol and left to dry in air.

The fabricated devices were morphologically characterized by scanning electron microscopy (SEM - FEI NOVA NanoSEM 400 microscope) and by confocal micro-Raman Spectroscopy (WITec Alpha-300R) equipped with a 50× microscope objective.

The Raman scattering spectra were taken at room temperature using the 532.0 nm laser wavelength (30 mW power) as the excitation source. All spectra were collected with 5 s integration time.

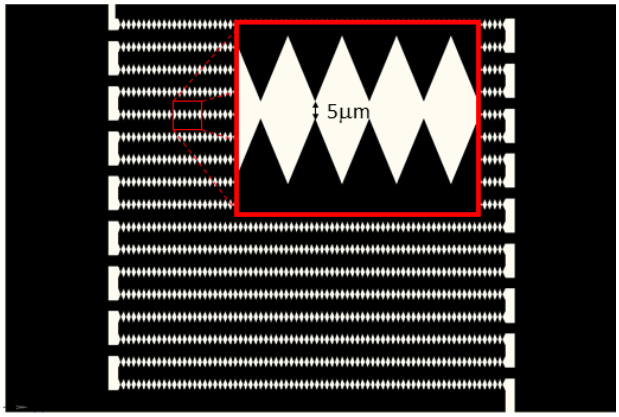


Figure 1. Interdigitated electrodes design for CNT deposition. The inset shows the minimum distance between electrodes, where CNT are deposited to form CNT "bridges" or "chains".

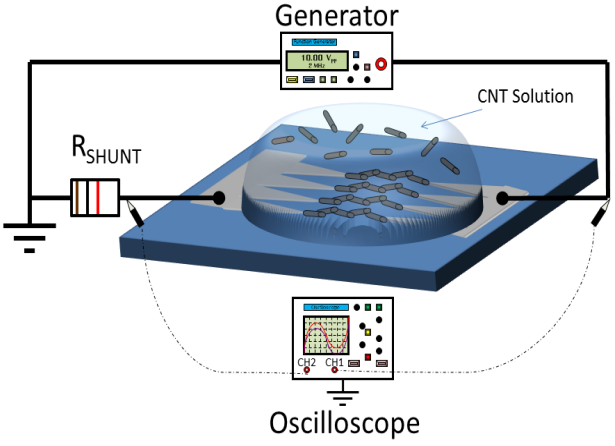


Figure 2. Setup for CNT dielectrophoretic deposition.

B. Electric Characterization

The devices were characterized before and after CNT deposition inside a controlled environment (dry N_2 and N_2 saturated with H_2O vapor), by using the experimental setup illustrated in Fig. 3. In this setup, the devices were inserted in a small-volume test chamber (300 μL), and the electrical measurements were performed with a Semiconductor Parameter Analyzer, model HP 4156A.

The humidity levels inside the chamber were established by simultaneously adjusting the fluxes of dry N_2 and N_2 saturated with H_2O through the needle valves and flow meters. The electromagnetic valves allowed controlling the time intervals of dry and humid N_2 injections.

The influence of the amount of MWCNT deposited on the device surface was verified by measuring the electrical conduction between the interdigitated electrodes. These characterizations were performed as follows: first, the devices were kept in dry N_2 environment to extract their I-V characteristics and to verify their ohmic or semiconductor behavior.

After that, their electrical resistances were monitored along time, while steps of dry N_2 (for 200 s) and N_2 + H_20 (for 20 s) were repeatedly injected into the test chamber. This procedure was adopted because humidity can considerably affect the charge carrier conduction in some materials. It is important to remark that the devices were also submitted to the same electrical characterization procedures before the CNT deposition to stabilize the Al electrode surfaces and avoid any additional oxidation during the tests with CNT.

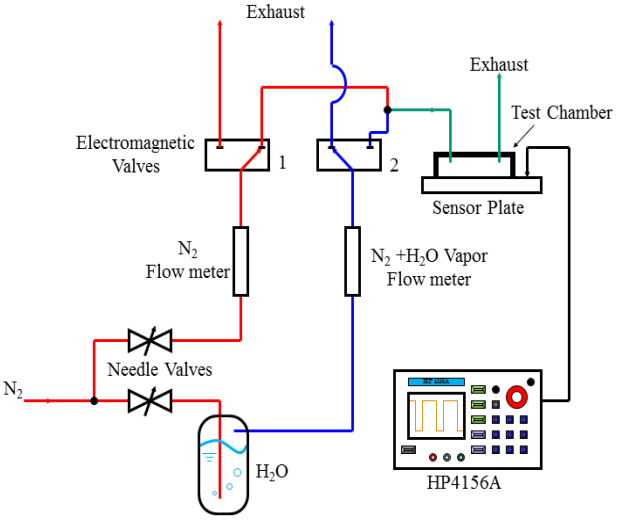


Figure 3. Experimental setup for the electrical characterization of the devices under dry and humid environments.

III. RESULTS AND DISCUSSION

A. Microscopy and Raman Spectroscopy

Fig. 4 shows the interdigitated electrodes defined by photolithographic process over glass substrate and the overall aspects of MWCNT DEP deposition for fabricated devices. These results indicate that the adequate choice of DEP parameters allowed obtaining controlled deposition of CNT with small amounts of material (Fig. 4c and 4d). In addition, they were preferentially deposited between the electrode tips, where the electric field is stronger, forming chains of nanotubes bonded to each other (Fig. 4e and 4f), as desired. Raman spectroscopy was carried out to evaluate the quality of carbon nanotubes or the presence of defects and amorphous carbon, as well as to identify eventual structural change related to the DEP time. Fig. 5 shows the Raman spectra obtained, which represent the general aspect for MWCNT [18] as expected, and no significant differences were noticed among samples.

The spectra are dominated by two peaks: the pronounced D band at ~1350 cm^{-1}, indicating the

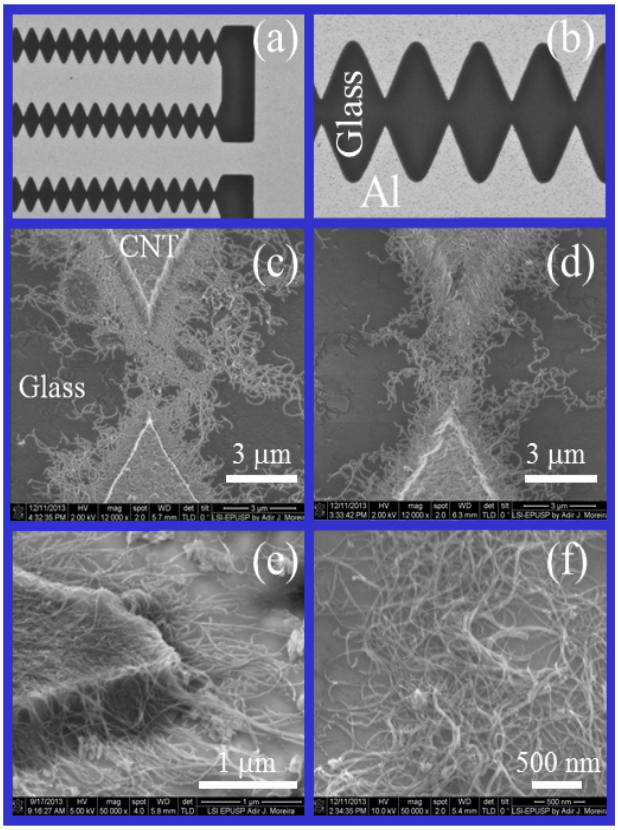


Figure 4. (a) Optical images of interdigitated Al electrodes. (b) Detail of Al electrode tips. (c) (d) SEM images of sample E30 showing the localized CNT deposition between electrode tips. (e) Detail of electrode tip with CNT deposited. (f) CNT deposited on the glass substrate by DEP.

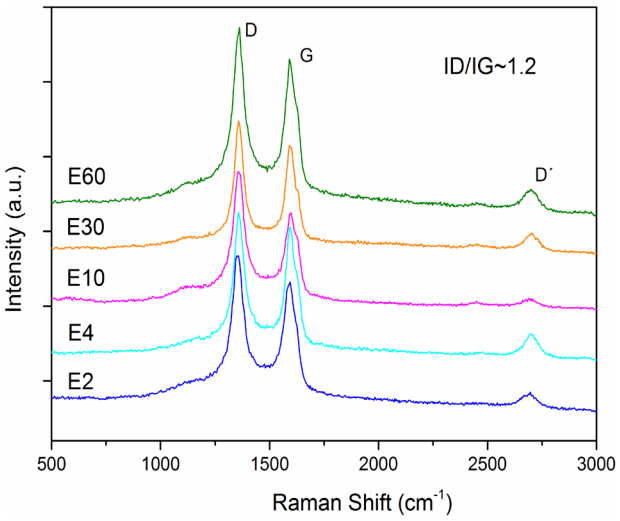
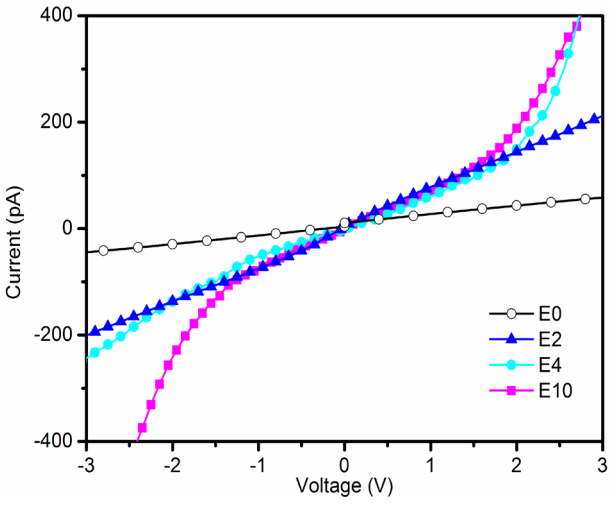
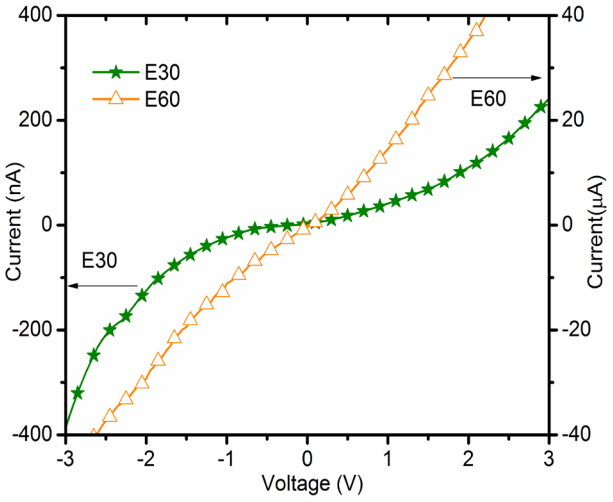


Figure 5. MWCNT Raman spectra for devices E2, E4, E10, E30, and E60. The spectra were obtained from MWCNT deposited on glass substrates near the electrode tips.

presence of some disorder, and the tangential G-band at ~1580 cm^{-1}, which is related to the lattice vibration of all carbon materials with sp^2 bonds. In addition, a discrete "shoulder" near 1620 cm^{-1}, called G2 or D´, was observed, which is a double resonance Raman feature induced by disorder or defects, similar to the D band. All samples also exhibit absorptions around 2700 cm^{-1}, which is assigned to the first overtone of the D mode and often called the Gl or 2D band [19]. The relation between D and G band intensities (R = ID/IG) was around 1.2 for all devices and this ratio is often used to evaluate the disorder density of the nanotube walls. R ratio close to or higher than 1 demonstrates high disorder due to abundant defects in the graphitic structure, which is usual for MWCNT [18, 19].



(a)



(b)

Figure 6. I-V curves for the devices in dry N_2: (a) E0 (without CNT), E2 (2 min. DEP), E4 (4 min. DEP), E10 (10 min. DEP). (b) E30 (30 min. DEP, left current axis) and E60 (60min. DEP, right current axis).

B. Electrical Measurements

The electrical behavior of devices was dependent on the amount of deposited nanomaterials as well as on the quality of their contacts. The current-voltage (I-V) curves of the fabricated devices are shown in Fig. 6. In addition, the I-V curve for the sample without CNT (device E0) is inserted as a reference. We verify a quasi-ohmic behavior for the device with little CNT deposition (DEP time of 2 minutes) with electrical resistance as high as the glass substrate resistance (device E0), but the behavior becomes non-ohmic when the CNT quantity rises (DEP time intervals higher than 4 minutes). The high electrical resistance measured (gigaohms range) for samples from 2 to 10 minutes of DEP time can be attributed to the low density of deposited CNT and the resistances in metal-CNT and CNT-CNT contacts. The nonlinear electrical behavior, pronounced for DEP time interval higher than 4 minutes, suggests the existence of contact resistances of metal-semiconductor interface type. The electron conduction increases significantly for large amounts of CNT deposited between interdigitated electrodes, as observed by the electric current levels shown in Figure 6b. Fig. 7 summarizes the electrical resistance measurements for all samples in dry N_2. The devices E30 and E60 present a significant resistance reduction: from hundreds of gigaohms before DEP to tens of megaohms for sample E30, and to hundreds of kiloohms for sample E60. On the other hand, devices processed with DEP time interval lower than 10 minutes present little electrical resistance variation when compared with the device without CNT. Based in these characterizations, we can assume that the CNT

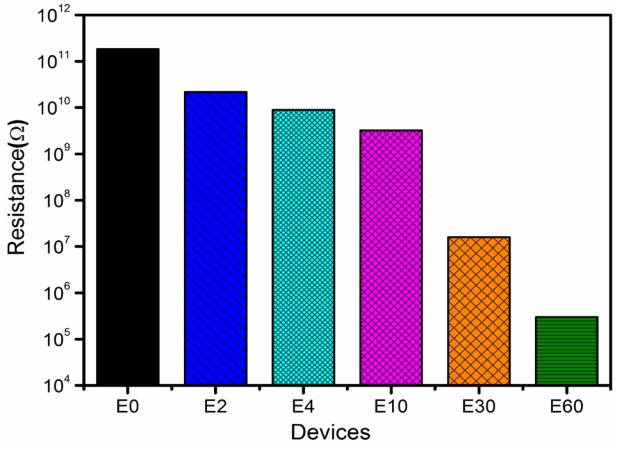


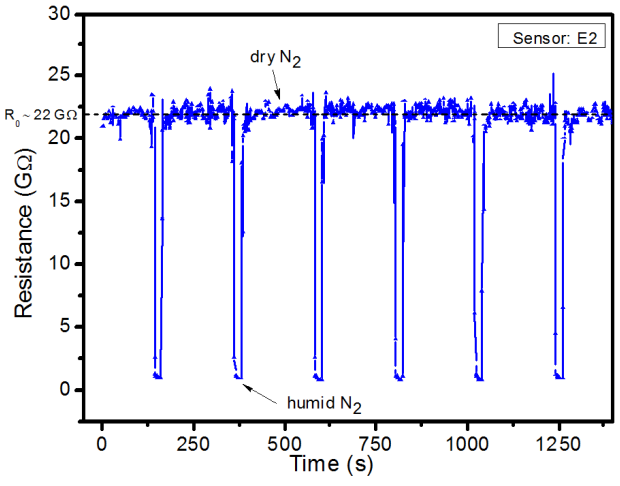
Figure 7. Measured resistances for devices into dry N_2: E0 (without CNT), E2 (2 min. DEP), E4 (4 min. DEP), E10 (10 min. DEP), E30 (30 min. DEP) and E60 (60min DEP).

"chains" between electrodes act as a resistor in parallel with the glass substrate. Therefore, as the deposited CNT amount rises, the equivalent resistance of this association decreases.

C. Humidity Sensing Properties

The electrical response of the devices was analyzed in humid environment according to the procedures described in section 2b to verify their potential use as gas sensors. Remarkable changes in electrical resistance in N_2 saturated with H_2O vapor environment were verified, as shown in Fig. 8. The response and recovery times, i.e., the time necessary to reach 90 % of total resistance variation for each step ("dry to humid" and "humid to dry"), were about only 7 s and 24 s, respectively (Fig. 8c). These results indicate that the interactions between water vapor and the devices are mainly dominated by physiosorption with weak bonds [15, 20, 21].

As it takes some time to break these weak bonds (probably due to the water molecules trapped in the CNT agglomerate), the total recovery times varied from 20 s (device E2) to 100 s (device E60). This result is important because it shows the relationship between the total recovery time and the amount of CNT deposited on devices. All the devices recovered their original resistive characteristics, and they did not show evidences of changes deriving from permanent oxidation or poisoning; thus, there was no need to heat or to expose them into vacuum environment, as reported in other works [22]. Possible Al oxidation [23], which could affect the response of devices along time, was considered negligible in our analysis because the devices were also exposed and characterized into oxidant environment before the CNT deposition, and no significant changes were noticed.



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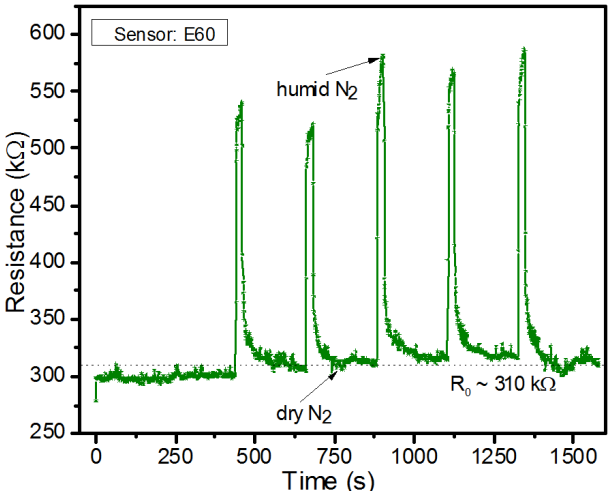

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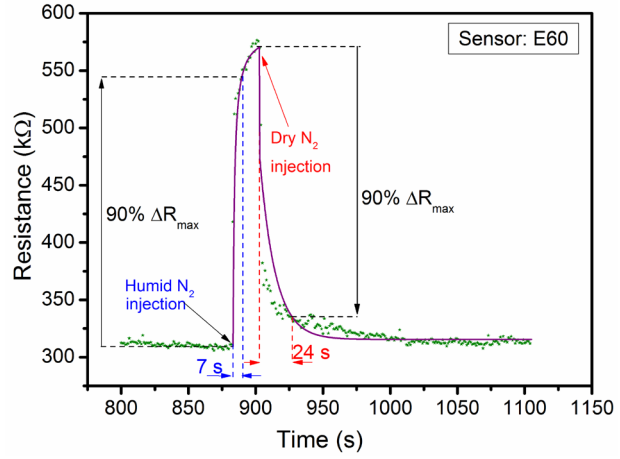

(c)

Figure 8. Dynamic electrical response of the devices (a) E2 (2 min. DEP) and (b) E60 (60 min. DEP) for steps: dry N_2 (200 s) and humid N_2 (20 s). (c) Detail of the E60 device response in the time range between 800 s and 1100 s for extracting response and recovery times.

Another evident aspect in Fig. 8 is the distinct behavior of resistance related to the DEP times applied. Fig. 8a shows the dynamic response for device E2 where a pronounced resistance reduction occurs when humid N_2 is injected into the chamber. However, an opposite effect was observed for sample E60: the resistance rises in the presence of injected humid N_2 (Fig. 8b). A possible mechanism to justify the E2 device resistance reduction is the electric conduction through water molecules adsorbed on the glass surface [24]. This effect was observed for the devices with little amount of deposited CNT (DEP times up to 10 minutes). This behavior is modified for devices with large amounts of CNT (as shown in Fig. 8b for device E60). In this case, the resistance increases in humid environment because the conduction mechanism is dominated by the CNT, which have p-type semiconductor behavior [25, 26]. Its resistivity tends to increase due to charge transfer from H_2O molecules to nanotubes, thereby depleting the hole density in the CNT [27].

Fig. 9 shows the relative resistance results (R_{humid}/R_o) for all the devices, where we can notice the gradual transition of their electrical behavior, and is related to the conduction mechanisms described. We can also assume that there must be a DEP time at which the resistances will not vary with humidity due to the equilibrium between both conduction mechanisms. This hypothesis will be the matter of future investigation.

Although the relative resistance variation of devices with little (E2, E4 and E10) or no (E0) CNT deposited is apparently higher, their absolute resistance values in the order of gigaohms are impractical for their association with usual measurement instrumentation. On the other hand, the E30 and E60 devices have absolute electrical resistances in the order of megaohms and kiloohms respectively. The E60 device presented the lowest sensitivity for humid N_2 ($R_{humid}/R_0 \cong 1.8$), but also the lowest absolute resistance, so we consider it the best device to explore practical implementations.

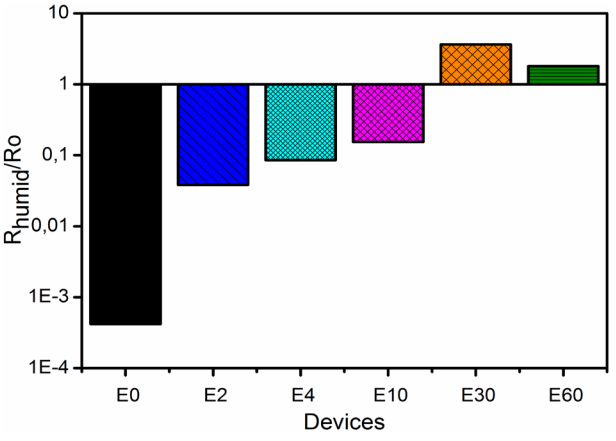

Figure 9. Relative resistances measured for devices into humid N_2: E0 (without CNT), E2 (2 min. DEP), E4 (4 min. DEP), E10 (10 min. DEP), E30 (30 min. DEP) and E60 (60min DEP).

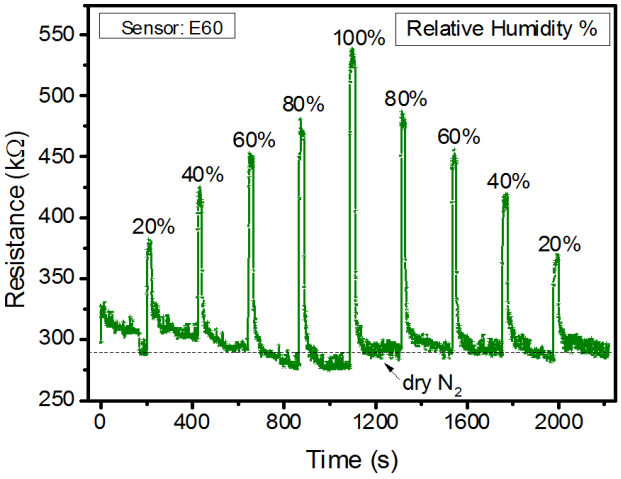

Figure 10. Device E60 response for 20%, 40%, 60%, 80%, and 100% humidity levels, as indicated.

Fig. 10 shows the evaluation of the E60 device for humidity level monitoring. This result suggests that a controlled amount of MWCNT deposited on glass substrates is potentially useful as a cost-effective alternative for humidity sensing.

IV. CONCLUSIONS

In summary, we report the fabrication of CNT resistive devices by applying DEP deposition of MWCNT over miniaturized electrodes on glass substrates. The electrode geometries and DEP parameters have allowed localized and oriented CNT deposition through the electric field established.

Raman spectra analysis presented the disorder degree typical for MWCNT, demonstrating that DEP processes do not cause damages or structural changes in the nanotubes.

Water molecules adsorbed on CNT surface increase the electrical resistance of this nanomaterial, but this effect can only be noticed in devices with large amounts of CNT. On the other hand, the electrical behavior is opposite if just little nanomaterial is deposited over glass substrate. In this case, the conduction is preferentially established through water molecules between electrodes.

All the devices fabricated presented sensitivity to humidity, but only sensors with large quantities of CNT are suitable for practical implementation as its absolute resistance is in the kiloohm range. The reduction of sensitivity verified for the sample with the highest DEP time must be a matter of future research.

Despite this reduction, the device was able to detect different water vapor levels through electrical resistance measurement at room temperature. All the sensors present fast response (response time around 7s for all the devices and recovery time from 20 s to 100 s), low drift and no evidences of permanent poisoning. These characteristics are very interesting for industrial applications.

The next steps will focus on the electrical behavior of these sensors in other gas environments to evaluate their sensitivity towards the development of integrated devices for several application fields.

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