Development of Fast Response Humidity Sensors Based on Carbon Nanotubes

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Abstract — **Current search on miniaturized humidity sensors primarily emphasizes issues related to integration and technological aspects. In this context, research efforts have been focused on developing sensors with Carbon Nanotubes (CNT) because of their promising sensing characteristics. However, there are challenges related to their application in commercial devices such as sensitivity, compatibility, and complexity of miniaturization, among others. In this work, we report the study of the electrical behavior of Multi-Walled Carbon Nanotubes (MWCNT) material deposited between interdigitated electrode structures by means of Dielectrophoresis (DEP), which is a simple and cost-effective method for deposition in micrometric regions. A fast and remarkable increase of electric resistance (up to 2.3 times) was noticed in the tested devices as a function of the concentration of water vapor, thus, these devices play an important and promising role for the development of integrated humidity sensors.**

***Keywords: Carbon Nanotubes, Dielectrophoretic Deposition, Humidity Sensors*.**

I. INTRODUCTION

Nanomaterials have been drawing a lot of attention from scientific community to their potential applications in several areas. Many efforts are focused on obtaining nanomaterials in large scale, or on the analysis of their physical and chemical properties, as well as their application in the technological area. Because of their interesting properties, they have stimulated the development of new gas sensors [1].

Among the various kinds of nanomaterials for humidity and gas sensing applications, Carbon Nanotubes (CNT) are interesting alternatives due to their remarkable characteristics such as high specific area, good electric conductivity, high mechanical and chemical stability [2]. In addition, their capability to change electrical characteristics at room temperature in contact with low concentration gases has been published in several works [3] [4]. Moreover, a lot of research has been focused on answering open questions about electrical conduction and sensing mechanisms of CNT [5] [6].

CNT can be divided essentially into two categories: Single-Walled (SWCNT) and Multi-Walled (MWCNT) carbon nanotubes. Although SWCNT present advantageous characteristics for electrical devices and gas sensors development due to their purity, experimentally MWCNT have been more attractive because they can be produced in large industrial scale, reducing the production cost in comparison with SWCNT. Various methods have been developed for integration or deposition of CNT over the surface of devices [7]-[9]. In particular, Dielectrophoresis (DEP) is a simple, versatile and cost-effective method to deposit and to align CNT on pre-fabricated electrodes immersed in solutions without post-processing procedures. Another advantage of DEP is its compatibility with existing microfabrication capabilities, because this process is conducted at room temperature, in noncorrosive solutions, and at low voltage. The Dielectrophoretic Force (F_{DEP}) arises when an external non-uniform electric field is applied between electrodes immersed in a CNT solution, inducing dipole moment in the nanotubes. The polarized CNT 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 when their permittivity (ε_p) exceeds the permittivity of the suspending medium (ε_m), otherwise they will be repelled. The CNT deposition by DEP method depends on other parameters such as amplitude, frequency, total time of the external applied voltage, CNT morphology, electrode geometries, and solution properties [10].

In this work, we investigate the electrical response of CNT deposited by DEP on interdigitated electrodes towards the development of integrated humidity gas sensors considering that commercial humidity sensors are usually big and slow. The search for fast and reliable sensors, integrated and compatible with microelectronic circuits is a current need. This paper is organized in four sections: Section I presents the advantages of CNT and the DEP process for humidity sensors development; Section II details the experimental procedure for devices fabrication and characterization; Section III shows and discusses the results of CNT deposition by DEP and the electrical characterization of the sensors in humidity environment; the conclusions and perspectives are described in Section IV.

II. EXPERIMENTAL PROCEDURE

A. Devices Fabrication

The fabricated devices were based on interdigitated electrode geometries [11]. Our devices are composed of two interdigitated aluminum (Al) electrodes (A and B), with five fingers each, deposited by sputtering over a planar glass

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substrate. As seen in the inset of Figure 1, each finger is composed of triangular geometries to concentrate the electric field during the DEP process and, consequently, to obtain CNT "bridges" between them. The minimum separation distance between electrodes is around 6 µm, and the CNT bridges will form parallel resistive elements between electrodes along the fingers.

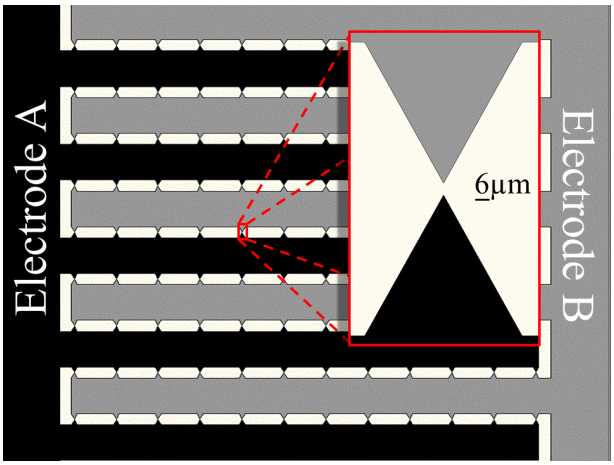

Figure 1. Interdigitated electrodes for CNT deposition. The inset shows the minimum distance between electrodes where CNT are deposited to form bridges.

The CNT used in this work were CVD-grown MWCNT (catalog n. PD15L520, from Nanolab Inc, USA), which were functionalized for DEP according to the protocols described in [12]. The CNT solution was applied directly onto the samples. The DEP CNT deposition was carried out with the setup illustrated in Figure 2, as follows: a sinusoidal signal with $V = 10\ V_{pp}$ and $f = 2\ MHz$ was applied for 60 minutes in the circuit by a function generator. A 1 $k\Omega$ shunt resistor was included to allow monitoring the DEP current and protecting the generator in case of short circuit in the electrochemical cell. The oscilloscope monitored the applied voltage and the current in the process.

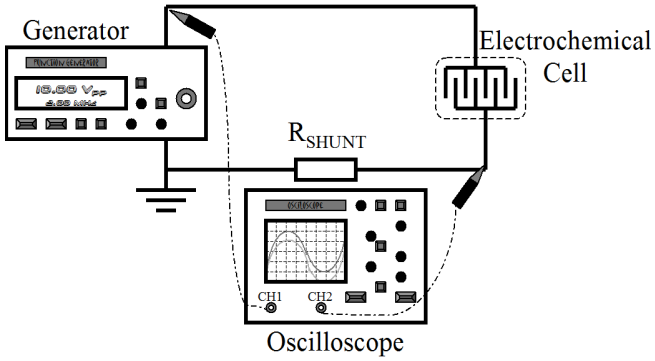

Figure 2. Setup applied for CNT dielectrophoretic deposition.

After the deposition process, the samples were rinsed in ethanol and left to dry in air. The fabricated devices were observed by Scanning Electron Microscopy (SEM) with a FEI NOVA NanoSEM 400 microscope.

B. *Electric Characterization*

All the samples were characterized before and after CNT deposition inside a controlled environment (from dry N_2 to N_2 saturated with H_2O vapor), by using the experimental setup illustrated in Figure 3 [13]. The N_2 was chosen as "background" environment to verify the sensitivity of the devices only for water vapor, avoiding the influence of other gas species. 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 into the chamber were established by adjusting simultaneously the fluxes of dry N_2 and N_2 saturated with H_2O through the needle valves and flowmeters. The electromagnetic valve allowed controlling the time intervals of dry and wet injections.

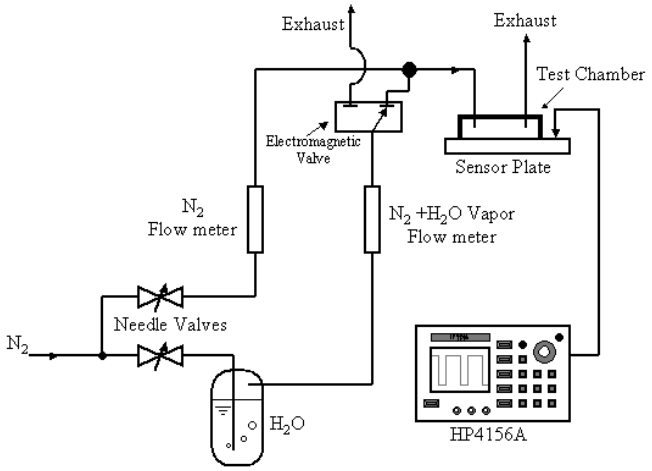

Figure 3. Experimental setup for electrical characterization of the devices under controlled humidity environments.

Before the humidity tests, the devices were dried into dry N_2 for several minutes. The influence of the deposited CNT was characterized by measuring the electrical resistance between the interdigitated electrode fingers. These characterizations were conducted as follows: first, the electrical resistances of the devices were monitored along the time by varying the humidity from 0 to 100% in N_2 environment (with steps of dry N_2 for 200 s and wet N_2 for 20 s). Second, they were submitted to injection steps of saturated wet N_2 to evaluate the response repeatability. It is important to remark that the devices were also submitted to the same electrical characterization procedures before the CNT deposition [13], with the aim to stabilize the Al electrode surfaces and avoid additional oxidation during the tests with CNT.

III. RESULTS AND DISCUSSION

Figure 4 shows DEP deposition aspects obtained on the devices. The results indicate the presence of CNT in several regions of the devices, but preferentially deposited at the apex of triangular geometries where the DEP electric field is stronger (Figures 4a and 4b). The applied DEP parameters allowed the formation of nanotube "chains" linked to each

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other; however, an inhomogeneous deposition among the electrodes was noticed (Figures 4c and 4d). The hypothesis for this inhomogeneity can be related to the nanotubes deposited in the beginning of DEP which could generate distortions in the applied electric field along the process. Then, the more CNT deposition, the more inhomogeneity could occur.

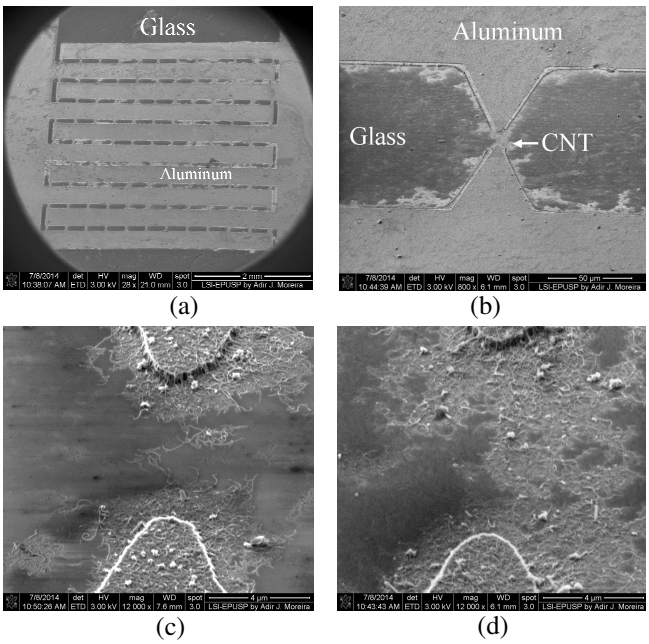

Figure 4. (a) Interdigitated electrodes after DEP CNT deposition; (b, c, d) Detail of CNT bridge between electrodes.

The devices presented a remarkable sensitivity to detect water vapor within a wide range of concentration. As shown in Figure 5, the device presented very fast increase and decrease of the resistance for humidity and for dry environment, respectively.

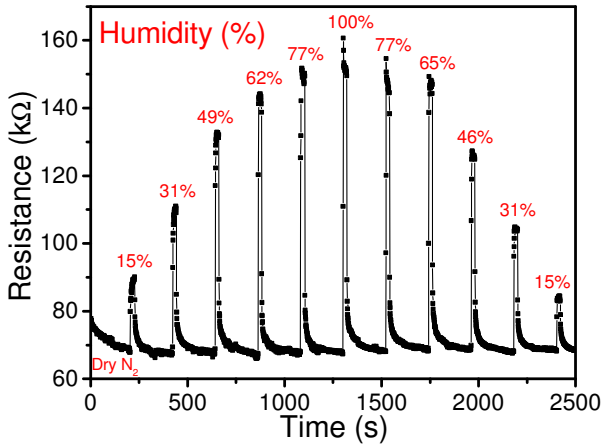

Figure 5. Device resistance along the time for several humidity conditions.

The response and recovery times are about only 3 s, i.e., the time necessary to reach 63 % of total resistance variation for each humidity level tested. This result indicates that the interaction between water vapor and CNT is mainly dominated by physiosorption with weak bonds. As it takes some time to break these weak bonds, probably due to the water molecules trapped into the agglomerated of the CNT, the total recovery time was about 90 s. The devices recovered their original characteristics, and they did not show evidences of changes occurred by permanent oxidation or poisoning, thus, there was no need to heat or to expose the devices into vacuum environment, as reported in other works [14]. The Al oxidation [15] 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.

The overall electrical response of these devices is the result of several CNT resistors in parallel configuration. Under dry N_2 environment, the resistance measured is related mainly to the existence of metal-CNT and CNT-CNT interface contact resistances [13]. The increase of this resistance in humidity environment occurs because the CNT have p-type semiconductor behavior, and its resistivity tends to increase due to charge transfer from H_2O molecules to CNT, thereby depleting the hole density in the CNT [16]-[18].

The devices showed repeatability of relative resistance measurements in the humidity range tested, with a well-defined trend. The relation between relative resistance R/R_0 and humidity shows no linear behavior (Figure 6), but the hysteresis is very low (about 7 %), which allow the devices to measure environments with increase or decrease of humidity levels with low dispersion. Results depicted in Figure 5 and summarized in Figure 6 show a clear correspondence between the device resistance and the environmental humidity. Naturally, additional careful measurements are needed to determine the accuracy and precision of the sensor.

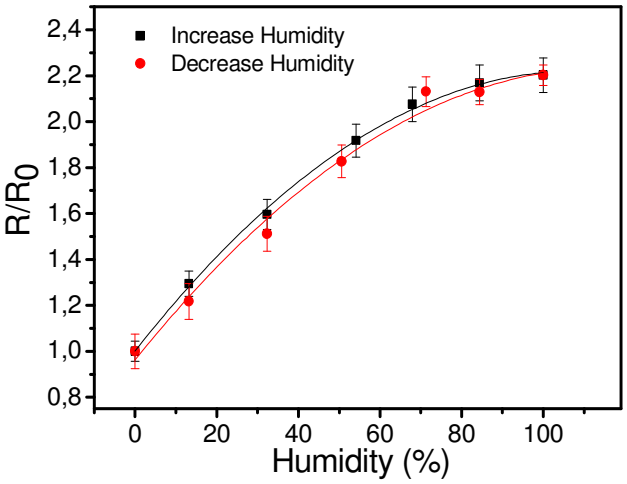

Figure 6. Relative resistance vs humidity for CNT device.

Figure 7 shows the response of the device for successive injections of water saturated N_2.

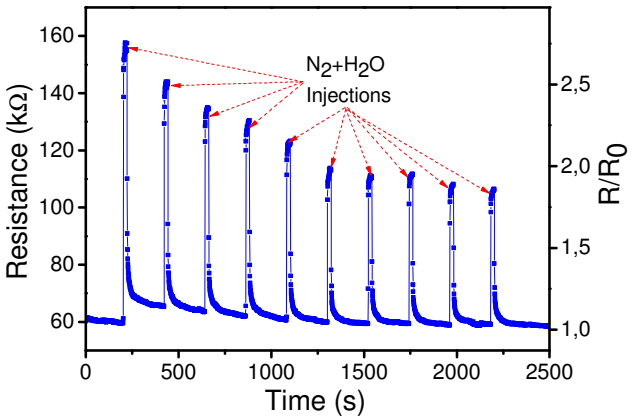

Figure 7. Electrical response for successive injections of humidity saturated N_2. Test steps: dry N_2 (200 s) and N_2 saturated with H_2O vapor (20 s).

One can verify a drift in the response, but it tends to stabilize after some injections. Moreover, the electrical resistance returns to the initial level because there is no sensor poisoning or significant oxidation of the electrodes after wet environment exposure, as described before.

IV. CONCLUSIONS

Miniaturized CNT resistive sensor devices were fabricated by applying DEP deposition. The electrode geometries and DEP parameters allowed CNT deposition preferentially localized. However, reduced DEP times must be experimented to promote CNT deposition only in the regions with stronger electric field. Water molecules adsorbed on CNT surface increase the electrical resistivity of this nanomaterial, and its value is dependent on water vapor concentration in the environment Experiments with other oxidant environments (including a background with synthetic air instead N_2) will be carried out aiming to obtain the selectivity of the sensors for practical applications. Although additional studies must be carried out to improve the sensors, they showed fast response, sensitivity even for low humidity level, and no evidence of poisoning, which is promising for the development of integrated sensors for industrial, agricultural and environment control applications.

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