Development of humidity sensors based on nanostructured carbon films

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Abstract

Humidity sensors based on clusters assembled nanostructured carbon films in capacitive configuration have been manufactured and characterized. An electronic read-out system has been designed and implemented in order to measure the complex impedance of the device under operation. Devices under test show a fast dynamic response and a good sensitivity compared to capacitive commercial systems. A linear response is observed for relative humidity in the range 2-70%. Hysteresis is practically absent in this range, while for higher values it is at most of the order of 2%.

Keywords: Nanostructured carbon; Supersonic Cluster Beam Deposition; capacitive humidity sensors

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1. Introduction

The measurement and control of humidity is an important and ticklish matter as water molecules are easily adsorbed on almost any surface, where they could be present as a mono-or multimolecular layer of molecules. The determination of humidity and moisture is thus imperative for improving quality of life and enhancing industrial processes. Commercial sensors are mostly based on metal oxides, such as Al$_2$O$_3$ [Rittersma review SA 96 (2002)] and TiO$_2$ [ref?]. Since now the advanced base-materials proposed for humidity sensing devices are porous silicon [4,5,Björkqvist et al, SA 112 2004, Das et al, SA A 94 2001] and polymers [6,7, Rittersma review]. In these materials the adsorption of water vapour drastically change the electrical properties of the device, which is usually in the form of a resistor or a capacitance. The investigation is focussed on the improvement of requirements as: short response time, high sensitivity, negligible hysteresis, resistance against contaminants, good long-term reproducibility and a possible large operating range for both humidity and temperature. All these requirements not always meet concurrently (or match each other). Low cost, easiness of manufacture and small-sized sensors are also required; so it has become mandatory to search for new materials fulfilling all these characteristics. Supersonic Cluster Beam Deposition (SCBD) can be used to grow nanostructured thin films where the original cluster structure is substantially maintained after deposition [1]. The random stacking of the precursor clusters leads to a high porosity texture, with a mesoscale granularity with pores in the range 20-500 Å and high specific surface areas [2]. The porous structure of this material suggests humidity sensing as a promising application [3]. Preliminary measurements performed by us on nanostructured carbon (ns-C) films equipped with electric contacts have shown that they are sensitive to relative humidity
In this work we discuss recent results on the development of ns-C humidity sensors in capacitive configuration, with particular concern to device geometry, design and manufacture of a suitable electronic read out system, tests in controlled atmosphere.

2. Experimental Procedure

The films have been produced by deposition of a supersonic beam of neutral carbon clusters at Dipartimento di Fisica, University of Milano, by using a pulsed microplasma cluster source (PMCS) [10, 11]. In a PMCS, an aerodynamically confined plasma discharge ablates a graphite rod; the vaporized carbon atoms are quenched in a condensation cavity by a pulse of helium and coalesce to form clusters. The helium-cluster mixture is then expanded through the source nozzle into a high-vacuum chamber (P~10^{-7}torr) to form a supersonic beam [11].

The sensor concept has been described in [9]. Sketches of the device is given in fig. 1a and 1b, while a picture of the manufactured sensor is shown in fig. 2.

Capacitance measurements have been performed by means of an electronic read-out system designed and manufactured at Dipartimento di Energetica, University of Firenze. The complex impedance \( Z_s \) of the sample is measured using the circuit described in fig. 3. An integrated waveform generator produces the sine voltage wave which excites the sample. The excitation frequency can be varied in the range 10-1000 kHz. The current flowing through the sample is converted into the voltage \( V_i \) by a transimpedance amplifier. The voltage drop across the sample is attenuated to obtain a signal \( V_V \) with the correct signal amplitude at the input of the Gain/Phase detector. The attenuating network is designed to introduce the same phase shift as the amplifier. The Gain Phase Detector performs the comparison between \( V_i \) and \( V_V \), producing two analog outputs: \( V_g \) and \( V_p \). \( V_g \propto V_V/V_i \) is proportional to the modulus of \( Z_s \). \( V_p \) is proportional to the phase difference between \( V_V \) and \( V_i \), and in turn to the phase of \( Z_s \).
The outputs of the Gain Phase Detector are finally read by a data acquisition board and transmitted to a personal computer for recording and processing.

Relative humidity has been monitored with a commercial hygrometer, consisting of a capacitive-type sensor produced by AHLBORN, Germany equipped with Almemo FH A 646-7 read-out electronics. Measurements have been performed in air with controlled humidity and temperature at atmospheric pressure. The apparatus (Fig. 4) consists of a humidifier and a small measurement chamber (volume: 405 cm$^3$). The relative humidity value is obtained by bubbling dry air in the humidifier, which contains distilled water and can be heated from 20 °C to 80 °C by means of a resistor. The relative humidity percentage inside the measurement chamber is controlled by two inlet needle valves. During measurements the relative humidity and the temperature of the sample are monitored. It is also possible to heat the sample in vacuum in order to achieve the complete desorption of residual water vapour molecules and thus to refresh the capacitive device. The evacuation of the chamber is performed by a diaphragm pump.

3. Results and discussion

Capacitance measurements have been performed for different relative humidity values, ranging from 2% to 90%. In fig. 5 capacitance vs relative humidity is shown. The starting point of the adsorption curve is 2 RH%, from where the RH was gradually raised up to 90% and then it was gradually reduced back to 2% to obtain the desorption curve. A linear behaviour up to 70% RH is observed, while a superlinear trend is observed for higher relative humidity values. In the range 2-80% no hysteresis is observed. In the higher RH% range a slight hysteresis is observed. Although more measurements would be necessary to quantify the effect, estimations suggest a 2%. From data sheets, a 1% hysteresis characterizes the commercial device. Fast and reversible changes in the capacitance have been observed as the
relative humidity is varied as it is evidenced in fig. 6, where capacitance vs time is shown. The dynamical response of the ns-C based sensor is compared to that of the commercial system, in adsorption and desorption regimes respectively in figs 7 and 8. The plots evidence the faster response of the ns-C sensor to humidity changes, as compared to the commercial system. The rising and falling times (calculated as the time to observe capacitance changes between 10% and 90% ) are of the order of 20s, similar to those of the commercial hygrometric system.

4. Conclusions
Capacitive humidity sensors based on nanostructured carbon produced by supersonic cluster beam deposition have been manufactured. The devices have been tested with an electronic system developed by us to measure the complex impedance of the sensor. An humidification set-up was implemented to cyclically measure the capacitance response of the device in the range 2-90% at room temperature and atmospheric pressure.

At constant relative humidity the capacitance of the ns-C sensor is stable and reproducible. The signal proved to be linearly dependent on relative humidity in the range 2-70%. For higher relative humidity values a superlinear trend is observed; a slight hysteresis effect is visible in the RH range 80-90%. Although more systematic measurements would be necessary to quantify the hysteresis effect, our analysis indicates that this should be at most 2%, against a 1% value certified for the commercial hygrometer.

A further engineering of the ns-C sensor is now under way to extend linearity in the whole RH% range and further reduce hysteresis. As superlinearity and hysteresis could be ascribed to water condensation inside pores [Gregg and Sing Adsorption, Surface area and porosity, Academic Press, Björkqvist et al, SA 112 (2004), …]; pore size is a key parameter to improve the overall sensing performance. Capillary condensation occurs for radii smaller then
the Kelvin radius $r_K$ [Gregg and Sing], which becomes smaller when the surface is more hydrophobic, i.e. for contact angles $> 90^\circ$. It has been already pointed out that an hydrophobic surface is achievable in our ns-C films by increasing the average slope of the surface, i.e. the steepness (and roughness) of the film surface [Ostrovskaia et al, Europhysics letters, 63, (2003) 401]. Film roughness is therefore another important topic to control sensors efficiency. To reduce the superlinear trend and hysteresis it could be also useful to heat the sample in order to avoid capillary condensation inside smaller pores: a constant temperature operation is nevertheless far more reliable for humidity measurements. A further engineered top electrode, as a small-mesh [Rittersma review], would also be considered in forthcoming works to further improve sensitivity and response times, and to uniform the electric field distribution in the active layer.
**Figure Captions**

Fig 1 (a) Sketch of the layers composing the capacitive sensor ; (b) sketch of the sensor structure.

Fig. 2 Picture of the capacitive sensor based on ns-C.

Fig. 3 Sketch of the read -out system manufactured by us and used to perform complex impedance measurements.

Fig. 4 Sketch of the humidification system

Fig. 5 Capacitance vs relative humidity curves in the range 2-90% RH

Fig. 6 Adsorbtion curves for ns-C sensor and commercial humidity sensor (AHLBORN-Almemo) as a function of the time

Fig. 7. Comparison of the dynamic response measured at room temperature of the ns-C based device and the (rising-edge).

Fig. 8 Comparison of the dynamic response measured at room temperature of the ns-C based device and the commercial humidity sensor (AHLBORN-Almemo) (falling-edge).
References


Fig. 1(a)

Fig. 1 (b)

Fig. 2

Fig. 3
Fig. 4

Fig. 5
Fig. 6

Fig. 7
Fig. 8
Biographies