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Use of a CNT-coated piezoelectric cantilever with double transduction as a gas sensor for benzene detection at room temperature

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Abstract

In this work, we propose to use a screen-printed piezoelectric cantilever with double transduction. Indeed, the piezoelectric cantilever is used as a resonant type sensor coated with carbon nanotubes (CNTs) as sensitive layer. Then, the resistance of CNTs is measured in static mode in parallel thanks to a modification of the cantilever top electrode. The combination of the CNTs equilibrium conductivity measurement and the resonance frequency shift of the 31-longitudinal mode allows the use of this device as a chemical gas sensor for benzene detection. The responses towards benzene concentrations under different relative humidity backgrounds are discussed.

Keywords: piezoelectric cantilever; double transduction; CNTs; 31-longitudinal mode; chemical gas sensor; benzene

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1. Introduction

It is known that thanks to their high sensitivity, resonant microcantilevers are used for many applications including gas sensor [1]. Au/PZT/Au cantilevers with sandwich electrodes are fabricated on an alumina substrate by associating the screen-printing technique with the sacrificial layer process [2]. Thanks to the piezoelectric effect, they integrate both self-actuating and self-read-out functions. Their basic principle is explained by a competition between stress and mass effect due to the adsorption of the target gas on the sensitive coating leading to a resonance frequency shift. Also, unlike in typical silicon cantilevers, a high frequency 31-longitudinal mode is used in order to

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reach higher sensitivity [3] for gas sensing application [4]. CNTs are good candidates as sensitive layer since they have high specific area (up to 1800 m^2/g in single wall CNTs) and the possibility to be chemically functionalized and metal decorated [5]. Moreover, the top electrode, which normally covers the full surface of the cantilever, has been replaced here by interdigitated electrodes. Therefore, in this new device, two transduction mechanisms are present i.e. changes in the resonance frequency and in the equilibrium conductivity of CNTs (translated into resistance shifts). This should help obtain more information from every measurement in view of better identifying/quantifying vapors.

2. Experimental and results

Au/PZT/Au cantilevers (2x8x0.1 mm^3) with sandwich electrodes (Fig. 1. a) are fabricated on an alumina substrate by associating the screen-printing technique with the sacrificial layer process. After each screen-printed layer, the alumina substrate is dried at 120°C during 30 min. Moreover, a microheater is screen-printed on the substrate prior to the cantilever processing for further studies on temperature effect and heat in experimental process. To improve sample's densification before firing, the dried layers are isostatically pressed at 40 MPa and 60°C during 4 min. Then the samples are fired 2 h at 900°C. Finally, dissolution of the sacrificial layer is performed in the H_3PO_4 aqueous solution at pH=1. For simultaneous resonance frequency shift and resistance variation measurements of the CNTs coating, the top rectangular electrode is replaced by two interdigitated electrodes as shown in Fig. 1. (b).

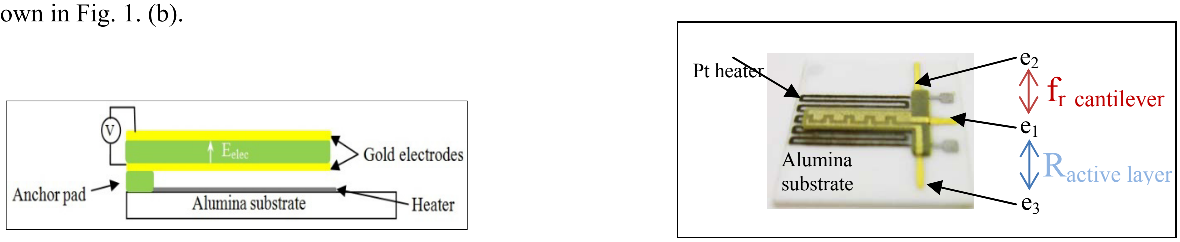

Fig. 1. (a) Self-actuated and self-readout PZT cantilever basic principle; (b) Double transduction method where the bottom electrode is e_2 and the interdigitated electrodes are e_1 and e_3.

Finally, to exhibit piezoelectric properties, the cantilever is progressively poled between the bottom electrode and the top electrodes (the latter are kept under short circuit). A maximum electric field of 55 $kV.cm^{-1}$ (value before dielectric breakdown) is increasingly applied under nitrogen atmosphere while the leakage current intensity is monitored to ensure it remains below 5 μA. The temperature is set at 280°C, just below the Curie temperature of PZT (see Fig. 2.). Then the system is cooled down while reaching and keeping constant the maximum electric field.

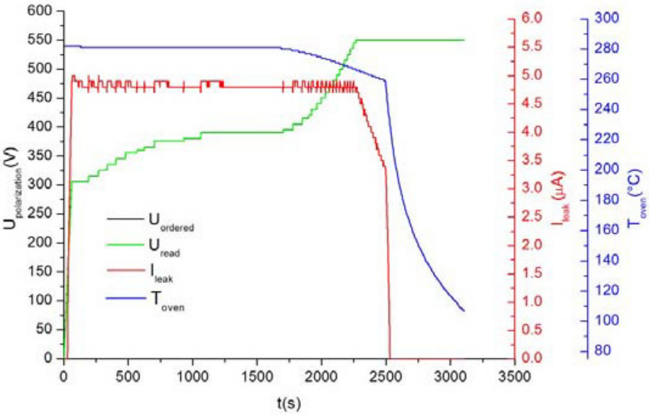

Fig. 2. Different parameters of the polarization step

The piezoelectric properties of this new cantilever measured with an Agilent E5061B impedancemeter show a resonant frequency $f_r \sim 70$ kHz and a high quality factor Q ~1700 for the first 31-longitudinal mode. The cantilevers are afterwards coated with CNTs by drop coating on the top gold electrodes shown in Fig. 3. (a). The CNTs are multiwall types obtained by chemical vapor deposition and functionalized by oxygen-argon plasma to improve their surface reactivity (named O-MWCNTs). The monitoring of the resistance of CNT films during the deposition is made to achieve resistances of a few decades of ohms. After the CNTs deposition, a negative resonance frequency shift of few hundreds Hertz is observed because of the predominant cantilever mass effect as shown in Fig. 3. (b).

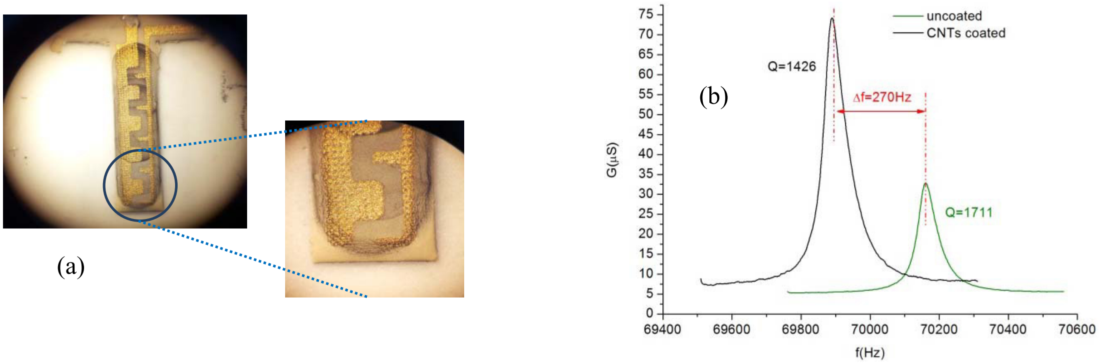

Fig. 3. (a) Optical microscope view of the CNTs drop coated, (b) Conductance of the PZT cantilever at the resonance frequency before and after CNTs deposition

The sensor is placed in a gas chamber (350 mm^2) and is heated at 150°C during 15 minutes in order to desorb contaminants from the cantilever. Then resonance frequency will be followed thanks to a dynamic working mode. First an average of the resonance frequency is measured from the conductance curve shown in Fig. 3. (b) and a fixed susceptance value is deduced. This value is always the same near the resonance frequency so a scan is performed each 8 seconds to follow the resonance frequency. Then, alternatively, the resistance of the CNTs film is measured at 1kHz in static mode (without cantilever vibration), since they show a resistive behavior at this frequency. All those parameters are controlled with a Labview environment. The gas flow and dilution are controlled with an Environics mass flow system employing calibrated gas cylinders and dry air as carrier.

First results show a positive shift of the resonance frequency due to a stress effect under benzene with low noise thanks to a high quality factor and a LOD ~ 2.8 ppm. The resistance shifts of CNTs shows a LOD ~ 50ppm (Fig. 4). The effect of relative humidity changes has been also investigated. Here negative shifts are observed due to the fact that a wide change in the relative humidity content has been studied (see Fig. 5.).

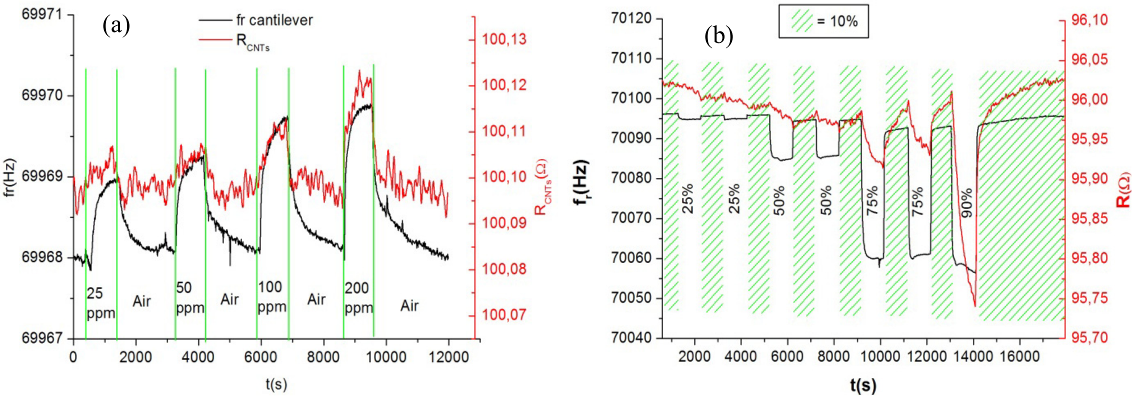

Fig. 4. (a) Response under benzene of CNTs coated PZT cantilever at room temperature and (b) Response under humidity of CNTs coated PZT cantilever at room temperature

3. Conclusion

It has been shown the fabrication and the use of a modified PZT cantilever with double transduction as a chemical gas sensor. Resistance signal of CNTs is noisy so deposition technique needs to be changed in order to have a better homogenous layer and improve sensitivity. Effect of humidity is significant, and further details like the detection of benzene in the presence of different moisture content will be investigated.

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