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COMMUNICATIONS

QUARTZ CRYSTAL MICRO– BALANCE GAS SENSOR WITH INK–JET PRINTED NANO– DIAMOND SENSITIVE LAYER

Pavel Kulha [*, **] **– Jiří Kroutil** [*] **– Alexandr Laposa** [*] **– Václav Procházka** [*, **] **– Miroslav Husák** [*]

Abstract — the paper presents fabrication and characterization of a Quartz Crystal Microbalance based gas sensor with a diamond powder sensitive layer deposited using the ink-jet printing technique. The sensor was exposed to a low concentration of ammonia, acetone vapors and different levels of humidity. Impedance characteristics close to the natural resonant frequency of 10 MHz were examined. The sensor exhibits significant shifts in serial resonant frequency under different gas environments.

Keywords: gas sensor, QCM, nanodiamond, ink-jet printing

1 INTRODUCTION

The quartz crystal microbalance (QCM) represents an extremely sensitive piezoelectric sensor (with capability to measure changes of the mass on electrodes down to nanograms) for detection of chemical and biological substances or to study nanoparticle self-assembly processes, nanocomposite materials and to track nanoparticle interactions in the environment [1]. High stability of the resonant frequency under various working conditions is required in many applications (timing and communication circuits) but in the case of sensing applications the influence of undesirable quantities on the resonance frequency must be studied. Since the early 20th century, quartz sensors have been used to measure temperature, pressure, force, acceleration, film thickness, fluid viscosity and other parameters. The change in mass on the resonator electrode due to adsorption of a certain gas on the selective layer is adopted in gas or chemical sensors. A big advantage of using QCM is very low power consumption compared to conventional metal oxide gas sensors with a power demanding heating system [2].

2 STRUCTURE OF THE SENSOR

For fabrication of the sensing element, both-side polished AT-cut (35° 15′) quartz crystal plates with a diameter of 14 mm and thickness 170 μm were used. Two key-hole shaped electrodes with diameters 5 mm were deposited on both sides by vacuum deposition. The electrodes were composed of a 30 nm Cr adhesion-layer and a 100 nm top Au layer. The mass sensitive area is situated in the central part of the resonator, covering the area where the two electrodes are overlapped, thus creating the thickness shear mode resonator (Fig. 1) [3].

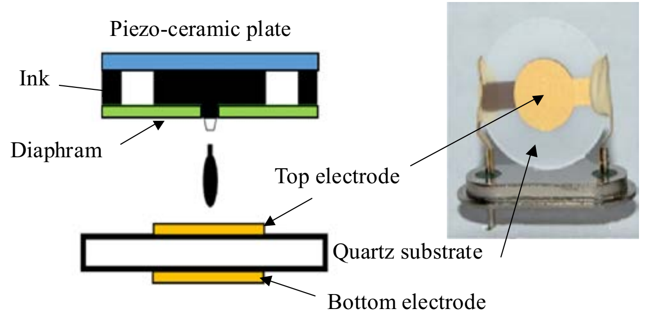

Fig. 1. Structure of the QCM sensor with a schematic drawing of ink-jet printing of a sensitive layer and a real sample mounted in HC-51/U package

3 DEPOSITION OF SENSING LAYER

Diamond represents a promising new material for many electrochemical and biological applications due to its inherent physical and chemical properties: extreme thermal and chemical stability, bioinertness and stable surface, which makes it a good candidate for gas- and biosensing applications [4].

Generally, ink-jet printing is a well-developed and inexpensive process by which liquid ink as well as solid suspensions in a properly formulated solution can be applied in a precise quantity and at selected locations on rigid or flexible substrates. Dimatix materials inkjet printer was used for selective printing of diamond powder. The volume of a single drop produced by the piezoelectric printer head is 10 pl. This allows printing of structures with resolution down to 40 μm with high reproducibility. The custom made ink was prepared as 12 mg of primary diamond particles (1–5 nm in size) suspended in 1 ml of ethyleneglycol [5]. The diamond remaining after ethyleneglycol evaporation created the sensitive area in the central part of the gold electrode (Fig. 1). The printed area on the

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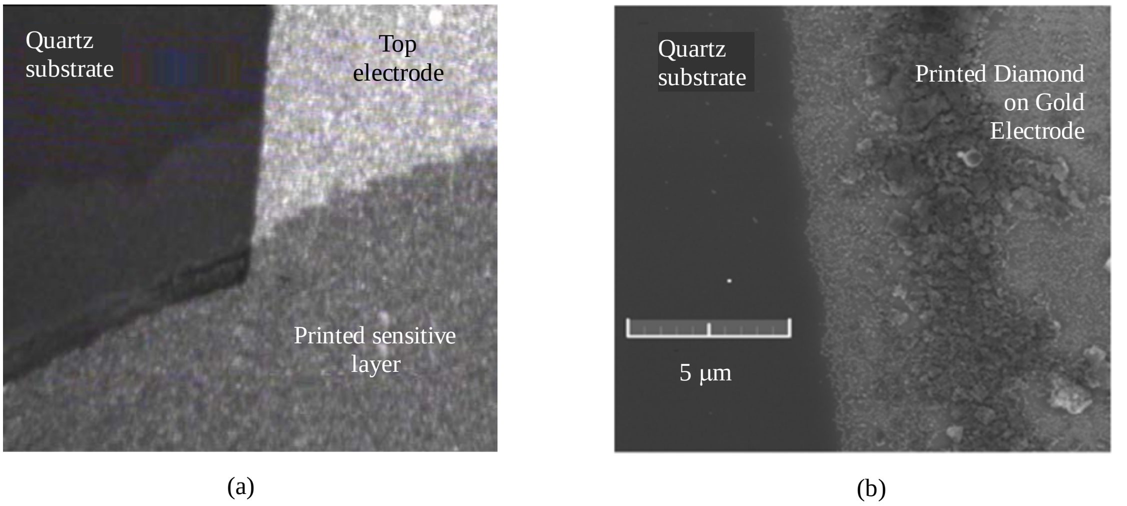

Fig. 2. (a) — Optical micrograph of the printed diamond-ethyleneglycol solution on the quartz substrate before evaporation, (b) — SEM image of printed diamond powder

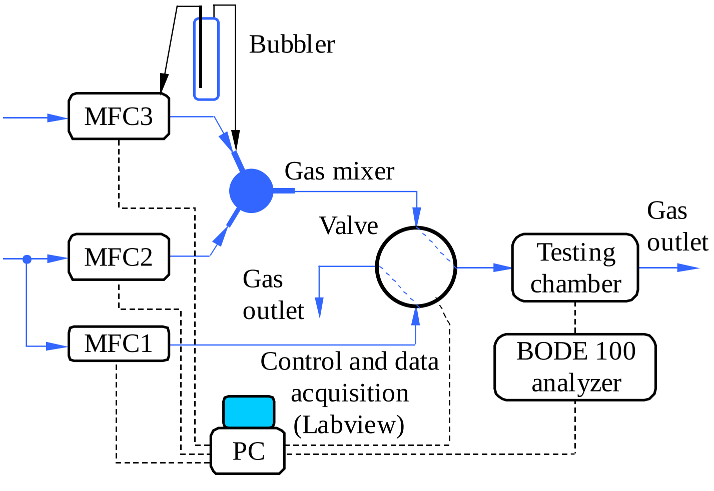

Fig. 3. Schematic drawing of the apparatus for sensor characterization

electrode was 20 mm^2. The as-printed ink before evaporation of ethyleneglycol is shown in Fig. 2a. Ethyleneglycol was evaporated using a hot plate at elevated temperature 50 °C for 15 min. SEM picture of the boundary between the printed and clean area is depicted in Fig. 2b. High clustering of diamond grains (visible close to the border of gold electrode) is caused by the coffee ring effect during evaporation of ethyleneglycol. The quartz resonator with the printed sensitive layer was then mounted into the HC-51/U package and contacts to the gold electrodes were fabricated using a silver nanoparticle conductive adhesive.

4 MEASUREMENT SETUP AND RESULTS

The sensors under test were characterized using a custom-made apparatus, detailed information on its capabilities can be found in [6]. The test procedure has two fundamental phases: the purging and the detection phases. During the first phase (purging) pure nitrogen gas flows through the test chamber to obtain a baseline. The stable level of the gas flow was controlled by a programmable mass flow controller. The detected gas concentration (NH_3) was controlled by mixing the ratio of NH_3 concentration in N_2. Acetone vapors and humidity level were produced using a bubbler and mixing with carrier gas (N_2).

The impedance characteristics of the tested sensors were examined using an Omicron Bode 100 — vector network and impedance analyzer. Frequency sweep measurement with center frequency close to 10 MHz at the first natural mode and a span of 4 kHz was performed. Shifts in the frequency of serial or parallel resonant frequency were examined in dependence on the concentration of the tested gas in the range of 50 ppm NH_3, $\sim$ 1 % acetone vapor, and different humidity levels. The sensor was tested under stable room temperature. Sample results of impedance characteristics and frequency shifts are depicted in Fig. 4.

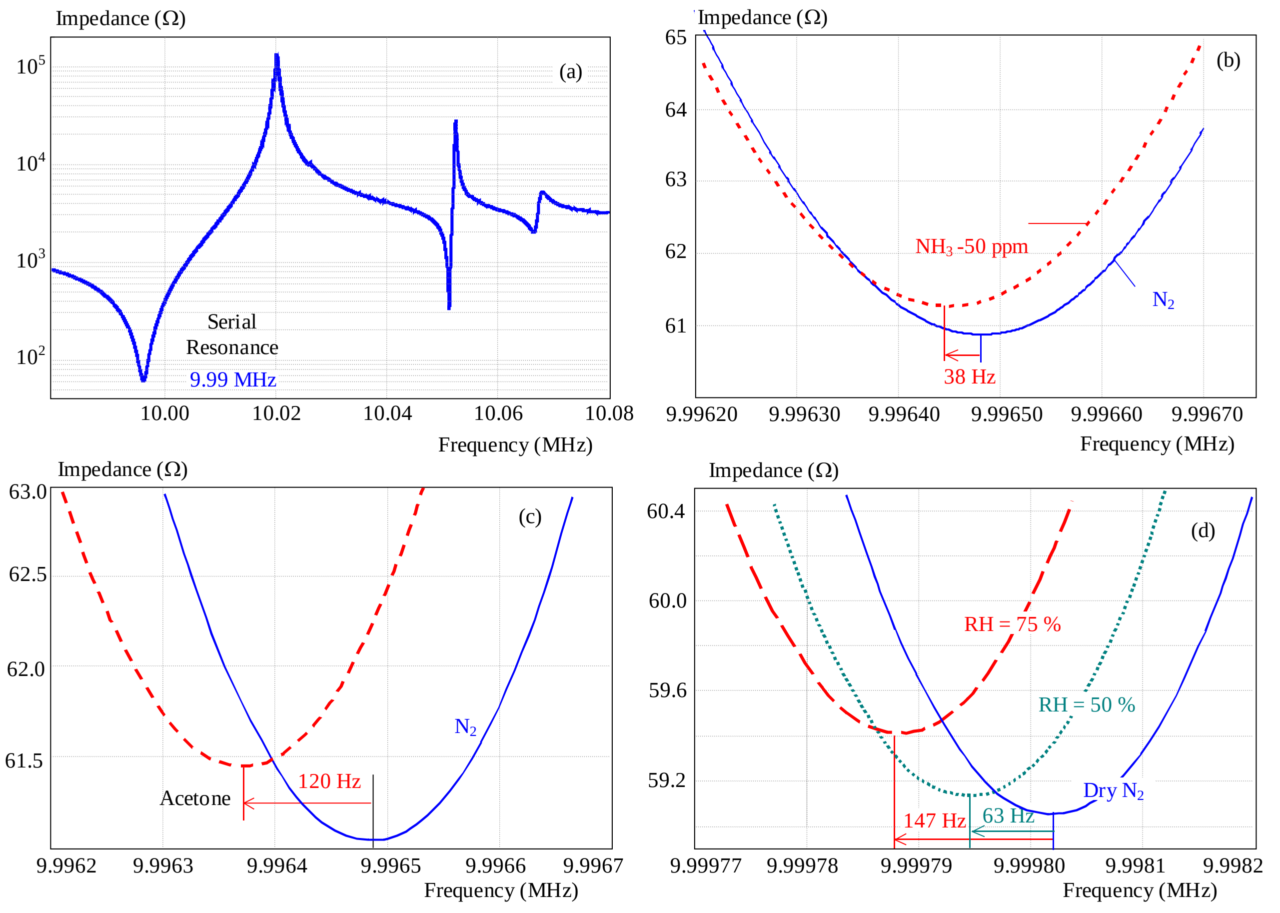

Fig. 4. (a) — Impedance characteristics of the sensor under test with a serial/parallel resonance peak and spurious modes; detail of shift in serial resonance after exposure to (b) — 50 ppm of ammonia, (c) 1 % of acetone vapour, (d) — change in relative humidity from 0 % RH to 75 % RH

Figure 4a shows the overall impedance characteristics of the sensor under test around 10 MHz (which is the first natural resonant mode) with a clear serial/parallel resonance peak and spurious modes. Detail of the shift in serial resonance after exposure to 50 ppm of ammonia is depicted in Fig. 4b. A shift in frequency of 38 Hz was observed. A shift of 120 Hz was observed for acetone vapor but the concentration is much higher (1 %). The sensor is also sensitive to humidity, frequency shifts of 63 Hz and 147 Hz were obtained for a change in relative humidity from 0 % RH to 50 % RH and 75 % RH.

5 DISCUSSION

The frequency shift of the resonator is directly influenced by adsorption of the gas molecules on the sensitive layer of the resonator electrode. The diamond surface is composed of nanocrystals, so due to its morphology it has a much larger area to adsorb more gas molecules compared to a flat surface. Good sensitivity to ammonia is given by the polarity of the NH_3 molecule with a free electron pair and affinity to the diamond surface. The frequency shift of 38 Hz for diamond based sensor is three times higher compared to the QCM sensor coated with ZnO sensitive layer reported by Nguyen *et al* [7]. The absolute frequency shift observed for acetone vapors was higher (compared to NH_3) but also for relatively high concentration of 1 %. QCM based devices are often used for detection of volatile organic compounds (VOC) but the sensitive layer is usually based on polymeric materials as polyaniline [8] that mostly exhibit higher sensitivity to VOCs. The largest shift in frequency of 147 Hz in our experiments was observed for changes of relative humidity in wet air. A higher sensitivity to humidity was reported by Yao *et al* [9] (up to 4 kHz @ 97 % RH) on QCM with an air-brush deposited nanodiamond sensitive layer.

6 CONCLUSIONS

A quartz crystal resonant gas sensor with a printed diamond powder layer was successfully fabricated and tested. The sensor exhibits a significant shift in serial resonant frequency for testing gases, especially for ppm concentration of ammonia. The tested technique of printing the diamond powder also opens a possibility for selective deposition of a nucleation layer for a further CVD diamond growth.

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