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Thermal resonant zeolite-based gas sensor

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ABSTRACT

New concept of microfabricated thermal resonant gas sensor comprising of a cantilever-like thermal device covered with a selective zeolite layer associated to heat feedback electronics is presented. Sensing principle exploits the thermal resonant frequency shift caused by mass variations upon gas adsorption in the zeolite layer; the proof-of-concept is demonstrated by selective adsorption of water and ethanol in hydrophilic FAU type zeolite layer. Hollow silicon supporting structures were fabricated in order to enhance the zeolite to silicon mass ratio, thus improving the relative thermal mass variation under gas adsorption.

1. Introduction

Micro-Electro-Mechanical Systems (MEMS) sensors with very high sensitivity and short response time have been studied for decades in order to miniaturize chemical devices [1]. The progress achieved in the field of miniaturized chemical sensors has been driven in large part by the development of micro-hot-plates or micro-calorimeters [2–8], and cantilever-based sensors [9–16].

Microcalorimeters exploit the extremely low thermal mass of MEMS sensors, which allows quick thermal cycles over several hundreds of Celsius degrees. The techniques [5] based on thermal analysis, either differential scanning calorimetry (DSC), differential thermal analysis (DTA), temperature programmed desorption (TPD) or thermogravimetric analysis (TGA), require the decomposition of adsorbed molecules [17] and/or their desorption as a function of temperature [2,5], while temperature ranges over hundreds of Celsius degrees are covered.

On the other hand, the detection principle of the mechanical cantilever-based gas sensor is based on resonance mechanical frequency shift of the cantilever due to mass change upon gas adsorption [14]. The frequency shift can be monitored directly through displacement measurement with external optical means [1,9] or indirectly with integrated strain gauge [11,15].

In this work, a thermal resonant zeolite-based gas sensor is presented. It is composed of a thermal device operated in closed-loop mode to form a thermal resonant structure. The resonant frequency depends on the thermal mass, *i.e.* the heat capacity, of the device. When gas adsorbs onto the device, the thermal mass increase results in a thermal resonant frequency decrease. The amplitude of the thermal oscillations, of several hundreds of milli-Celsius degrees, does not involve desorption or decomposition of adsorbed species.

The adsorption selectivity is ensured and demonstrated with zeolite layers deposited on the device. This method is compatible with batch fabrication and suitable for further miniaturization.

Selectivity of MEMS gas sensors can be provided by either organic or inorganic layer coatings [15]. Porous material and particularly zeolites reveal great chemical, size and shape selectivity controlled by variation of chemical composition (hydrophilicity/hydrophobicity), pore dimensions, crystal size and orientation within the layers, thus enabling detection and differentiation between different gases and vapours.

2. Principle of operation

The sensing device consists of a thermal device associated to an electronic heat feedback system as illustrated in Fig. 1. The thermal device comprises a thermally insulated part, linked to its environ-

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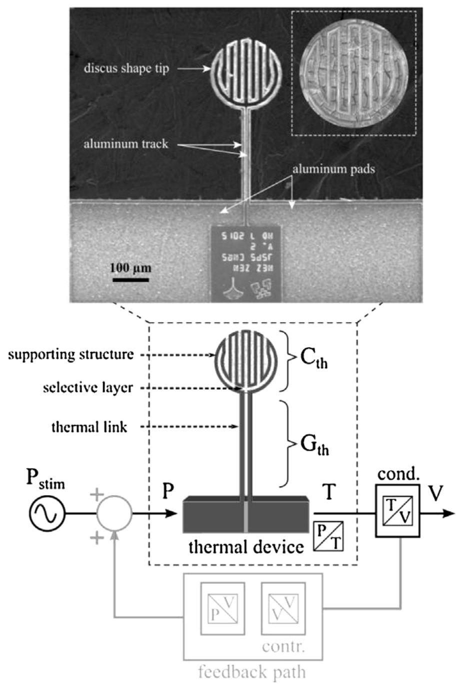

Fig. 1. Thermal device principle (bottom part): the thermal device turns power variation into temperature variations [P/T]. The conditioning electronics monitors the temperature of the device through resistance measurement of the aluminum-conducting track [T/V]. A feedback path with a controller enables the heat feedback [V/P] required for closed-loop mode operation. Scanning electron microscopy (SEM) pictures of the structure (top part): an SEM image of a micro-fabricated silicon (250 µm beam and 200 µm diameter) discus tip structure with a thickness of 9 µm; the single aluminum track serves as both the heater and the temperature sensor. Inset: the tip filled with FAU-type zeolite.

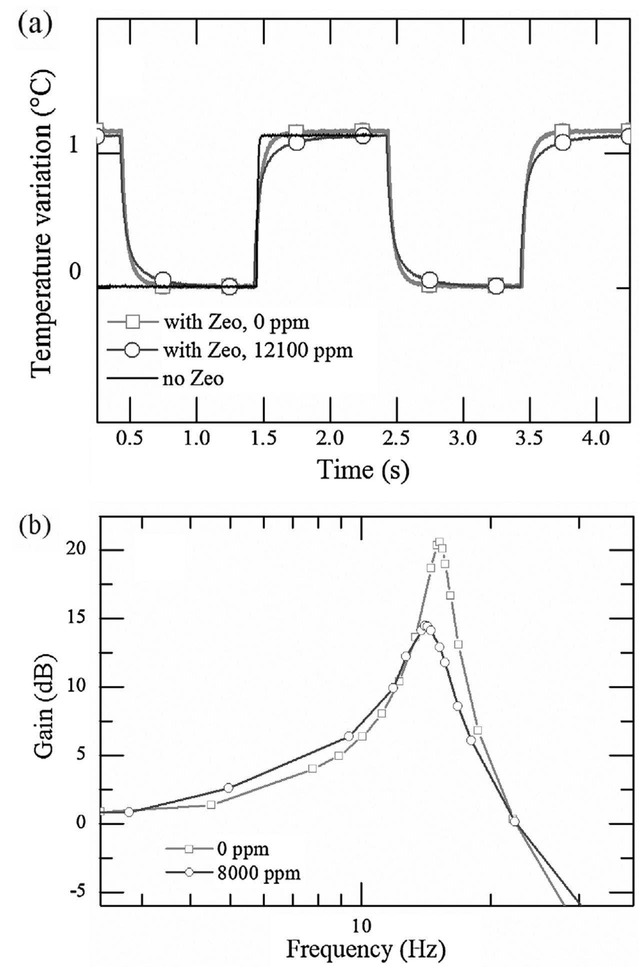

Fig. 2. (a) Temporal output temperature response of the thermal device covered with zeolite (with Zeo) in open-loop mode to square shape power stimulation upon the introduction (blue circle marked curve) under water vapor and free of water (red, square marked curve); the black curve stands for the reference structure without zeolites (no Zeo); (b) Gain of the thermal resonant device, closed-loop mode operation, upon the introduction (blue, circle marked curve) or not (red, square marked curve) of water vapor. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ment by a weak thermal link. The thermal mass of this thermally insulated part, C_{th}, associated to the thermal conductance of the weak link, G_{th}, forms the first order thermal system with a thermal time constant, $\tau_{th} = C_{th}/G_{th}$. When gas selectively adsorbs onto the zeolite layer, the thermal mass of the thermally insulated part increases. The thermal mass variation can be monitored through the variations of the thermal time constant of the system as previously reported [18].

Here, the thermal system is derived into a resonant thermal system, and thus the adsorption of gas relying on the shift of the thermal resonant frequency is monitored. A feedback path with a controller is associated to the thermal device to form a second order thermal system, which can be tuned into resonance. The thermal resonant frequency, as for mechanical resonant devices, varies with the square root of the variation induced by gas adsorption (gas mass in the case of mechanical resonant device, gas thermal mass in the case of thermal resonant device), $f_{res\_th} \propto 1/\sqrt{\tau_{th}} \propto 1/\sqrt{C_{th}}$. The operating principle is similar to the one of mechanical resonant gas devices but in the heat and temperature domains. The stimulation force in mechanical devices is replaced by heat power, while displacement oscillations in mechanical devices are replaced by temperature oscillations.

3. Description of the thermal device

The new sensor device, resembling a cantilever with a circle shape tip was microfabricated from silicon-on-insulator (SOI) wafers with one single aluminum-conducting track forming a circular serpentine (Fig. 1). The aluminum-conducting track is used for both heating and temperature sensing with the capacitively coupled electrical substitution principle [19,20]. The single track enables lowering the thermal conductance of the cantilever to the bulk with less metal and narrower supporting beam. The aluminum-conducting track had a resistance of 25.6 Ω and a TCR of 3.6×10^{-3}/K. The silicon supporting structure (sensor device) has a dimension of 9 µm thick and 200 µm diameter. This sensor device is filled with zeolite nanocrystals by drop-casting technique: FAU-type zeolite with a particle size of 10–20 nm was prepared according to the procedure described elsewhere [21]. The hollow silicon supporting structure enhances the zeolite to silicon mass ratio, thus improving the relative thermal mass variation under gas adsorption. The thermal mass of the silicon structure was 0.5 µJ/K without zeolites, and 3.6 µJ/K with zeolites at ambient conditions (extracted from temporal response of the device to power stimulation as illustrated in Fig. 2a). A silicon beam, 250 µm long and 15 µm wide, links the supporting structure to the bulk silicon and it acts as the weak thermal link with a thermal conductance of 60 µW/K.

4. Experimental set-up

The set up involves two thermal structures: (i) the first one is not covered with zeolite layer, and serves as a reference, and (ii) the second one is covered with zeolite layer and serves as a measuring selective device. The thermal resonance was measured in