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A New Approach in the Field of Hydrogen Gas Sensing Using MEMS Based 3C-SiC Microcantilevers

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Abstract. This paper demonstrates the ability of 3C-SiC microcantilevers (µCs) to monitor binary gas mixture without sensitive coating. Here, 3C-SiC is chosen in particular, as the newly designed sensor will be placed in a radioactive environment. The change in gas concentration is identified using relative shifts in the cantilever's mechanical resonance frequency (Δf_r). The presented microcantilevers work on electromagnetic actuation and inductive detection. In this paper, the fabrication process, optical characterization results using laser Doppler vibrometry and test results under a gas mixture environment are demonstrated. The presented limit of detection shows the ability of 3C-SiC-µCs to detect less than 1% of hydrogen in nitrogen, which makes them suitable for the targeted application.

Introduction

Currently, nuclear energy is the major source of electricity in many countries. In France, nuclear power plants produce three-fourth of the electricity [1]. Despite the objective of lowering nuclear energy production in France at 50% in 2035, it is necessary to safeguard the presently generated medium active with long life (MA-LL) and highly radioactive (HA) wastes with great care. Hence, the French National Radioactive Waste Management Agency (ANDRA) has been constructing a special disposal facility, 500m below the surface of the earth, to handle and store them properly [2]. Among these nuclear wastes, the presence of large quantities of metallic materials will lead to the formation of hydrogen (H_2) gas. This is due to corrosion in an anoxic medium (corrosion by water in absence of oxygen). To mention, H_2 at concentrations between 4% and 75% in volume of air, is highly flammable. Therefore, monitoring the presence of H_2 concentration within this facility becomes mandatory to avoid any potential explosion.

Generally, the conventional gas sensors are coated with sensitive materials to absorb the analyte of interest. In case of H_2 sensing, it is often coated with metal like palladium or platinum [3]. The main disadvantages of these sensors are fast aging, long response time and low reliability. Therefore, the first set of microcantilevers (µCs) without sensitive coating for the targeted application were fabricated with familiar silicon (Si) material. The mentioned study was used to analyze and differentiate the influence of geometries and dimensions of cantilevers in the gas environment [4]. However, the Si-based MEMS devices are not applicable to survive in hostile environments (here radioactive, high temperature and corrosive) because of their premature degradation [5-6]. Hence, we have chosen silicon carbide (SiC) to replace Si. Knowing that SiC has remarkable physical and mechanical properties over conventional materials [7-8]. After the work of Tayeb *et al.*, we upgraded the choice of material, i.e. SiC, with proposed rectangular geometry. In our study, we choose the cubic polytype of SiC that allows us to grow 3C-SiC(001) thin films epitaxially on cheap Si(001) substrates.

The paper is divided into multiple sections, in which the first section explains the fabrication process of 3C-SiC-µCs. Second section demonstrates the optical measurement using laser Doppler vibrometry (LDV). Finally, as a proof of concept, the gas detections were performed for low and very low concentrations of H_2 in nitrogen (N_2) using inductive detection.

Fabrication of 3C-SiC Microcantilevers

The process flow to elaborate 3C-SiC-µCs is shown in Fig. 1. The epi-wafers used to fabricate the microcantilevers contain a 10µm-thick 3C-SiC(001) film heteroepitaxially grown by classical two-step growth process (carbonization followed by epitaxial growth) on 2-inch Si(001) substrate, with classical thickness of 275µm. In the first step (a), only alignment crosses were defined by etching 300nm of 3C-SiC epilayer. The second step (b) involves patterning and etching of 3C-SiC epilayer, to define the cantilevers geometry. Here, the entire height of the 3C-SiC epilayer was etched, as the microcantilever will be completely made of 3C-SiC (refer Fig. 1.b). Then, a thin film of undoped silica glass (USG) was deposited and patterned. This 200nm oxide layer insulates the substrate, i.e. 3C-SiC(001)/Si(001), and contact metals used for detection and actuation. In step 4, gold (Au) of 300nm was deposited for both detection and actuation metals. Moreover, a thin layer of titanium (Ti) was deposited between USG and Au to improve adhesion. Step four (d) is the final process in front-face micromachining. The last step (e) was releasing 3C-SiC-µC by anisotropic etching of Si(001) along (111) crystallographic direction from the rear side, using 20% of potassium hydroxide (KOH). Further, the fabricated cantilevers were packaged on specially designed printed circuit boards (PCBs) and were taken for further characterizations in air and gas mixture environments.

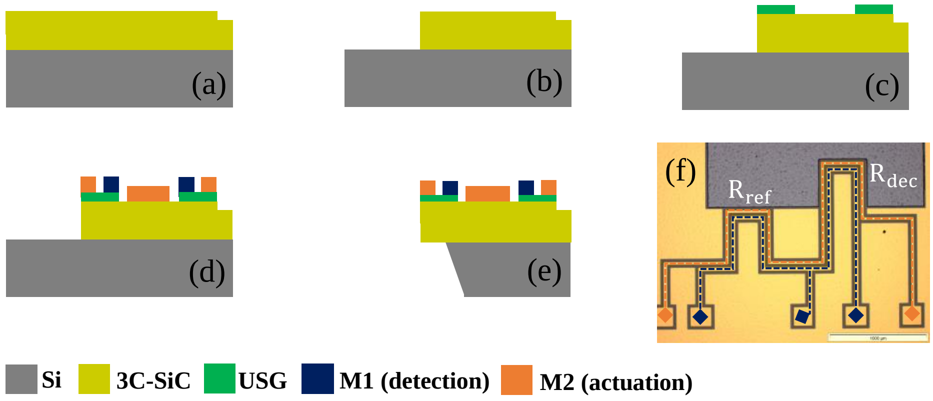

Fig. 1: Systematic process flow of 3C-SiC-µCs fabrication. (a) Patterning alignment crosses, (b) defining cantilevers geometry, (c) introduction of insulation layer to separate the substrate and the metal contacts, (d) deposition of metals for inductive detection and electromagnetic actuation and (e) releasing of cantilevers from rear side by wet etching the Si(001) using KOH. (f) Optical microscopic image of single 3C-SiC-µC showing the metal tracks of detection and actuation circuits.

Optical Characterization of 3C-SiC Microcantilevers Using LDV

The laser Doppler vibrometry is a non-contact assessment. The main goal of this optical characterization is to extract the mechanical resonance frequency (f_r) and the quality factor (Q) of the fabricated microcantilevers. In order to perform this experiment, the cantilever beam of interest was placed under the laser source and excited using the built-in wave generator of the Polytec MSA500 vibrometer. Here, a prototype was chosen arbitrarily to carry out the first set of characterization. The selected cantilever was of square shape and has a dimension of 500*500*10 μm^3.

By actuating the cantilever, the velocities for a range of frequencies have been measured. This was caused by Doppler shift from the reflected laser beam due to the motion at the examining area. The cantilever working principle is based on Laplace law, where the current $\left(\vec{I}(t)\right)$ in the circuit, due to applied voltage (V_{act}), induces a mechanical force $\left(\vec{F}(t)\right)$ in presence of a contact magnetic field $\left(\vec{B}\right)$ imposed by the magnet, as shown in Fig. 2. This measurement confirms the electromagnetic actuation mechanism of the microcantilevers by showing a clear resonance peak at its resonance frequency (f_r), for applied voltage. To mention, the detection metal track contains two different resistors, namely R_{ref} and R_{dec}. The R_{ref} was the reference resistor situated in the stationary part of the cantilever and R_{dec} was the detection resistor placed on the cantilever beam to detect change in motion by applying various gas concentrations for applied V_{act}.

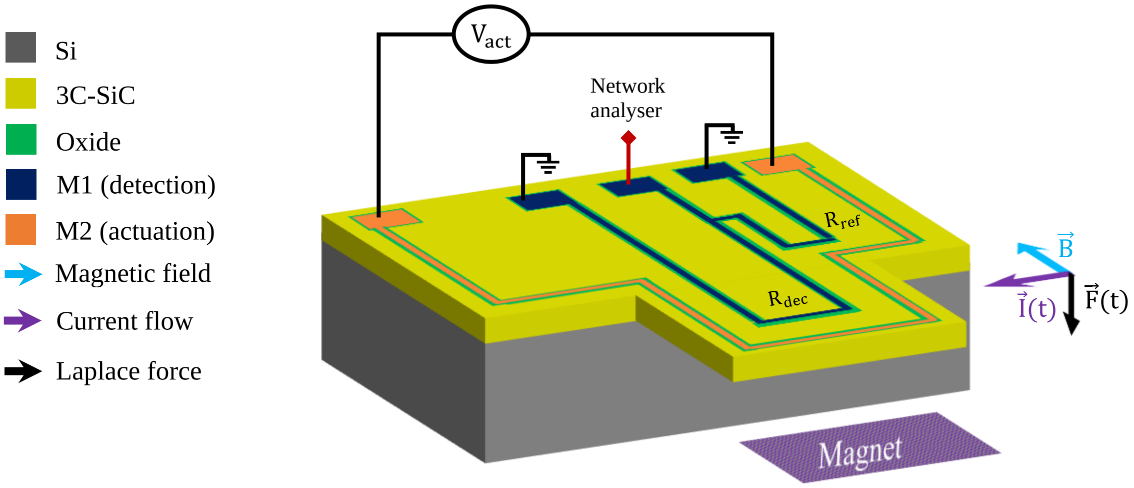

Fig. 2: Schematic of 3C-SiC-µC based hydrogen sensor without sensitive coating: a conductive gold wire is placed over the edge of the cantilever for electromagnetic actuation; the center point in detection metal track is connected to network analyser for measuring the relative change in resonance frequency for respective change in gas concentration caused by induction in the detection resistor.

With the measured velocities, the cantilever displacement for a range of frequencies were deduced. An example illustrating this is shown in Fig. 3, for various applied voltages. The measured f_r and calculated Q for the presented cantilever are 28.55 kHz and 357, respectively.

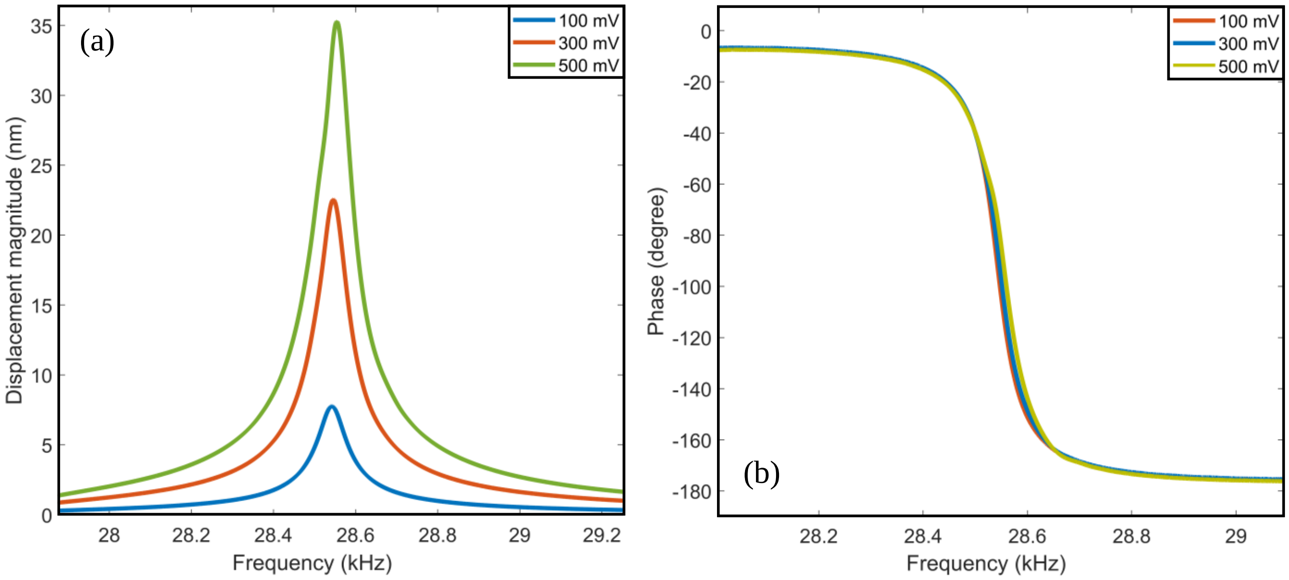

Fig. 3: Measured (a) displacement amplitude and (b) phase at various applied voltages for the selected microcantilever geometry.

Testing of 3C-SiC Microcantilevers under Gas Mixture Environment

To perform binary gas mixture analysis, a microcantilever chip prototyped on PCB was placed in the hermetic cell, which allowed the gas to flow during measurement. After making necessary electrical connections, as shown in Fig. 4, the microcantilever was actuated at 500mV. Then, lower concentrations of hydrogen with nitrogen were introduced in the hermetic cell. Here, N_2 was used as a reference gas. The gas flow was controlled using the LabVIEW program developed by IMS laboratory, Bordeaux. Similarly, the resulting shift in resonance frequency for changes in gas concentrations were recorded in another PC.

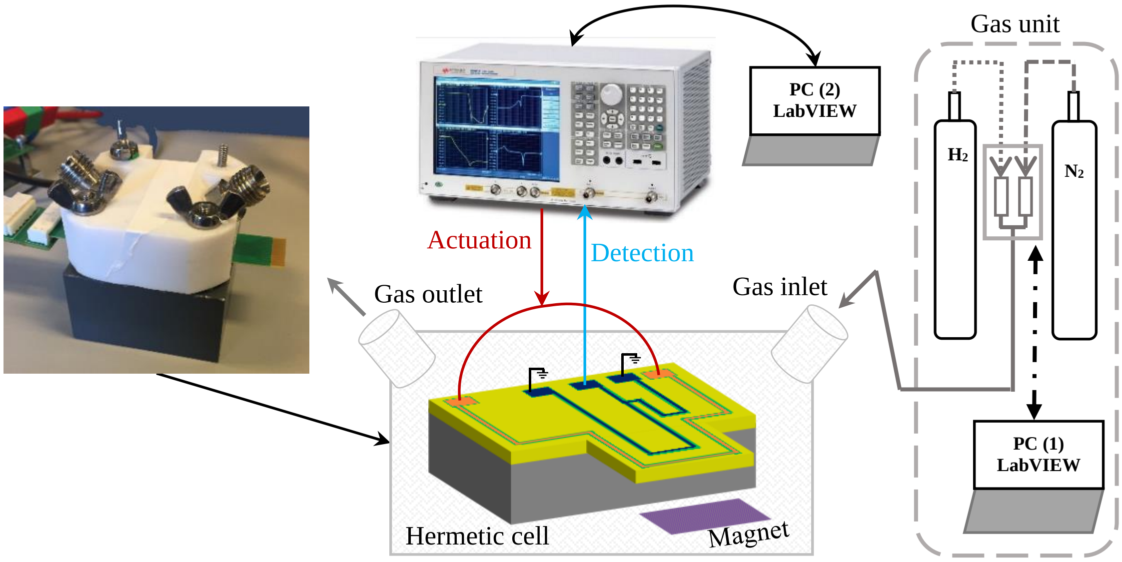

Fig. 4: Schematic of experimental protocol to measure the shift in resonance frequency for various gas concentrations under binary gas mixture environment, developed by IMS laboratory.

Firstly, the gas analysis was carried out for low concentrations of hydrogen, i.e. between 4% and 1%, to validate the system functionality. The results are displayed in Fig. 5.a. Here, the gas concentration was varied for every 5 min with 100% of nitrogen to reset the measurement. After the successful measurement of H_2 in N_2, the gas detection for very low concentrations (less than 1% of H_2 in N_2) have been performed. This limit of detection result shows that the tested sensor could detect 0.2% of H_2 in N_2 with non-optimized geometry and emission parameters.

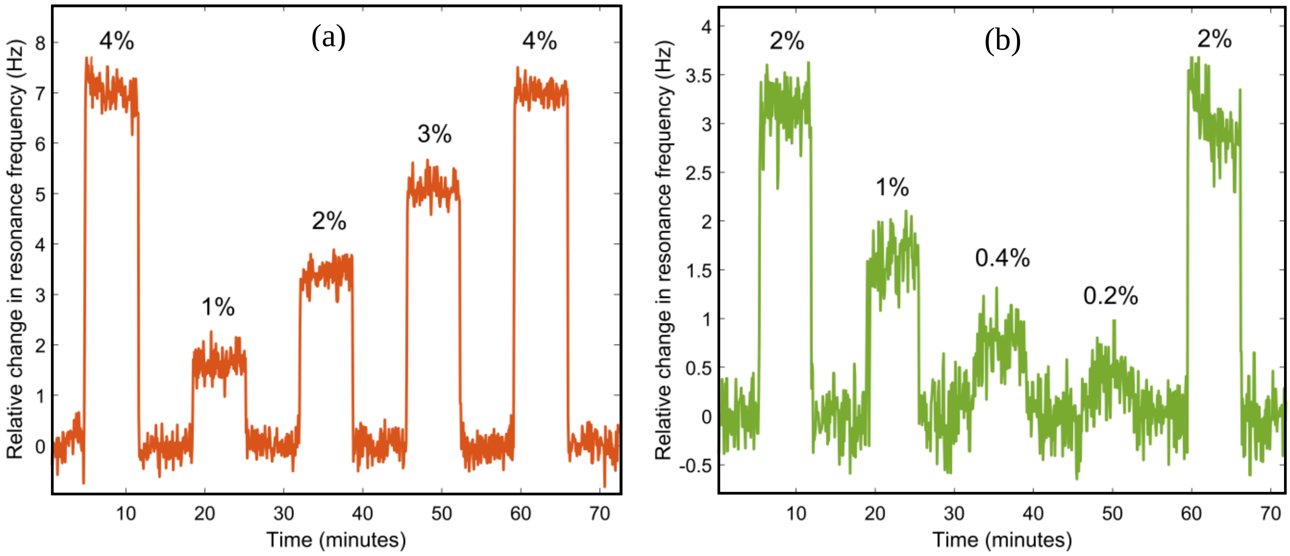

Fig. 5: Obtained relative shift in resonance frequency for (a) low concentration (1% to 4%) and (b) very low concentrations (less than 1%) of H_2 in N_2 with the presented geometry at V_{act} of 500mV.

Moreover, both graphs indicate that the resonance frequency increases as hydrogen concentration increases. This is because hydrogen is lighter than nitrogen. For instance, the resonance frequency will shift in the opposite direction, i.e. in negative values, for carbon dioxide in nitrogen, as CO_2 is denser than N_2. To mention, the densities of H_2, CO_2 and N_2 are 0.089 kg/m^3, 1.977 kg/m^3 and 1.250 kg/m^3 respectively at standard temperature and pressure (0 °C and 1 atm) [9].

Summary

The aim of the presented study was to fabricate a microsystem that can detect the presence of hydrogen in a radioactive environment. This goal has been achieved using the proposed 3C-SiC-µCs. After fabrication, these devices were characterized in air. Primarily, optical characterization was performed with a laser Doppler vibrometer. Through this measurement, the mechanical resonance frequency and the quality factor of each cantilever was determined. Further, the concept of using 3C-SiC-µCs as a hydrogen gas sensor without sensitive coating was validated by conducting tests under a hydrogen environment. The obtained results were very promising with a limit of detection of 0.2% for H_2 in N_2. In future, one could possibly attain a better LOD with optimized geometry and excitation parameters. Further, signal processing techniques should be incorporated to enhance the quality of the resulting signal. This set of preliminary results are promising to use 3C-SiC-µCs as a potential gas detector in harsh environments, due to their physical properties.

Acknowledgement

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