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3C-SiC MEMS for gas detection

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Abstract

Gas sensors are devices that can detect and/or discriminate gases in their surroundings. Usually, these kinds of sensors are based on vibrating structures with a coating sensitive to the species to detect, that can cause device failures issues like ageing, low reliability and high response time. Widely spread in commercial applications, these sensors are also of importance for industrial environments where they must be able to operate in harsh environment.

In this contribution, we present uncoated silicon carbide microsystem devices for gas detection. Limits of detection as low as 0.2% has been reached, illustrating the capabilities of such structures. In addition, thanks to the physical properties of this material, it can operate in severe conditions.

Introduction

Usually, the active structures of Micro-Electro-Mechanical-Systems (MEMS), which can be bridges, beams, or membranes, are mostly completed using silicon (Si), or related materials such as silicon nitride for example. But, with these materials, depending on the type of application targeted, it may be necessary to associate a cooling system or a shielding against radiation to the device. These additional elements add volume and weight, which is in complete contradiction with the desire for miniaturization sought for MEMS. Moreover, in fields such as space or aeronautics, an increase in weight leads to a drastic increase in costs [1].

Thanks to its properties, these problems can be circumvented by using silicon carbide (SiC) to achieve MEMS devices. Indeed, this material presents attractive physical properties, such as its resistance to radiation or its chemical inertness. These particularities make it an ideal candidate for the elaboration of MEMS devices.

Among the various silicon carbide polytypes, contrary to what is observed for the elaboration of electrical devices where 4H-SiC is largely used, the cubic silicon carbide polytype (3C-SiC) is perfectly suitable to address MEMS applications [2]. Indeed, since this polytype can be heteroepitaxied on Si substrates, most of the technological steps developed for silicon can be used to complete SiC-based MEMS using 3C-SiC.

In the literature, different fields of application have been addressed with SiC-based MEMS, but typically with a resonator as a common point, which can be lateral [3] or vertical [4]. For this type of application, the benefit of using SiC is justified by its mechanical properties. Actually, based on the Young's modulus of this material, the resonance frequencies are about 40% higher than those obtained with an equivalent Si-based device [5]. It can lead to key improvement, for example in the field of Atomic Force Microscopy where the resolution of the measure is closely linked to the resonance frequency of the beam [6]. Cantilevers can also be used as a tool, for example to determine the Young's modulus of the material involved [7]. In addition, thanks to both chemical inertness and radiation resistance, silicon carbide is compatible with harsh environments.

In this paper, we present the fabrication and the use of 3C-SiC-based MEMS devices to address gas detection applications, without functionalized coating. The purpose of removing the sensitive layer is to obtain more reliable and robust sensors with no need to calibration during the sensor's life cycle.

Experimental

At first, 3C-SiC thin monocrystalline films are grown on (100) silicon wafers using a conventional two steps process by means of Chemical Vapor Deposition (CVD) technique [8]. The growth is done in a homemade horizontal hot wall resistively heated reactor, using a mixture of propane and silane as gas precursors diluted in hydrogen (H/Si ratio ~ 2500) at 200 mbar. After *in situ* silicon surface preparation at high temperature, SiC nucleation is initiated under propane at 1070°C (carbonization) followed by an epitaxial growth stage under propane and silane at 1350°C, with C/Si ratio close to unity. For the purpose of the study, grown films have a thickness close to 10 μ m. After growth, a Chemical-Mechanical-Polishing (CMP) treatment is done to obtain a final surface roughness (Ra) below 1nm.

These 3C-SiC/Si(100) epi-wafers were used for the microcantilever fabrication, using 6 photolithographic steps, from creating the alignment patterns to release the cantilevers from the rear side of the silicon substrate, as summarized on Fig. 1 [9].

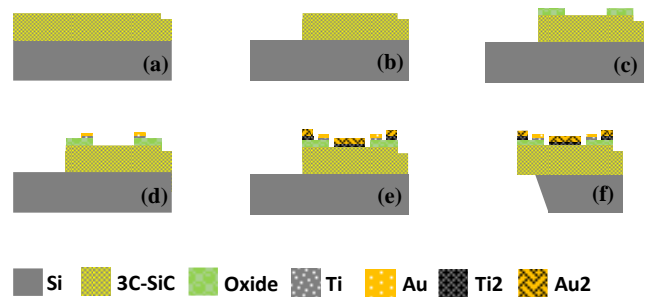


Fig. 1. Schematic process flow of 3C-SiC cantilevers fabrication, composed of 6 photolithographic steps: (a) patterning alignment crosses, (b) defining cantilevers geometries, (c) introduction of isolation layer to separate 3C-SiC and metal contacts, (d) metal deposition for inductive detection, (e) metal deposition for electromagnetic actuation and (f) cantilever releasing from rear side, by etching the Si substrate.

Following this 6-stage process, the electromagnetic actuation and inductive read-out cantilevers, as schematised on Fig. 2, were completed.

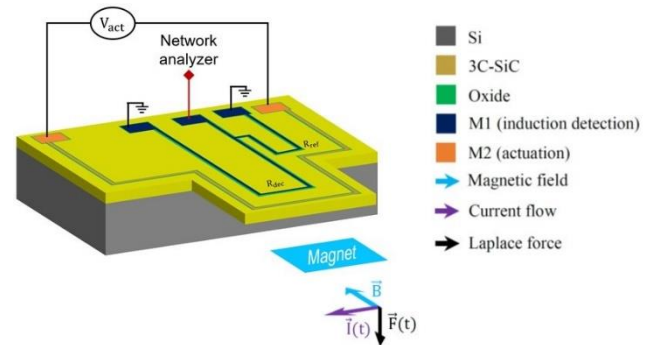


Fig. 2. 3C-SiC-based microcantilever using electromagnetic actuation and inductive detection, for gas detection.

The SiC microcantilever chips were diced and prototyped to carry out further electrical characterization and gas mixture analysis. The chips were glued on specially designed printed circuit boards (PCBs). Afterwards, the glued chips were baked at 150°C for one hour, to improve the adhesion between the PCB and the chip. Then, wedge bonding was performed using a 25µm diameter aluminum wire. The prototype, composed of 4 cantilevers, is presented in Fig. 3. Each SiC cantilever of this prototype typically has a 500µm length and a 500µm width, as it has been previously demonstrated that uniform rectangular cantilevers are more suitable for mass density measurement than the other tested T- and U-shapes [10]. Moreover, wide and short beams are more sensitive to the mass density variation; with the sensitivity of the rectangular beams being proportional to b/L^2 (b and L are the width and the length, respectively), as predicted by an analytical modeling [11]. For these dimensions, the resonance frequency and the quality factor of the 3C-SiC cantilevers, in air, are 28.55kHz and 357 respectively.

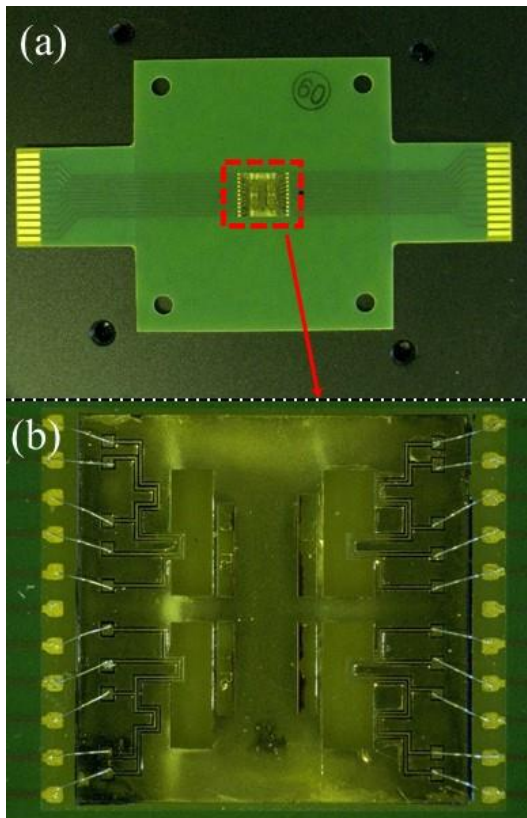


Fig. 3. (a) Fully packaged prototype and (b) optical microscopic view of wedge bonded 3C-SiC cantilevers on PCB, using 25µm diameter aluminum wires.

The prototype was then placed inside a hermetic cell which allows the gas flow during the measure, and the structures were measured under different gas mixtures. The experimental protocol is illustrated in Fig. 4. The gases are provided from industrial grade bottles and mixed using flowmeters, monitored by a computer, to reach the targeted concentrations.

Due to very small variations of resonant frequency that must be detected, new characterization methods for measuring small resonant frequency variations have been developed. The conventional method for monitoring the resonant frequency shift consists of searching for the resonant peak on the amplitude spectrum and tracking the change in the corresponding frequency. But the relative variation of the resonant frequency, in the case of low concentration of hydrogen (H_2) in nitrogen (N_2), is very small. For instance, using a silicon microcantilever (length = 1 mm, width = 1 mm and thickness = 10 µm, resonant frequency approximately 23 kHz), a concentration of 0.2% of H_2 in N_2 corresponds to a resonant frequency change of approximately 0.25 Hz, that means

a variation of only 10 ppm on the resonant frequency. Therefore, the conventional method does not prove to be sufficiently accurate to measure such a small shift in resonant frequency. This is mainly due to the difficulty of identifying precisely the resonant peak location due to the measurement noise. Consequently, different characterization methods using gain and phase spectra have been tested on measurement data [12] and used for the gas detection presented in the following sections.

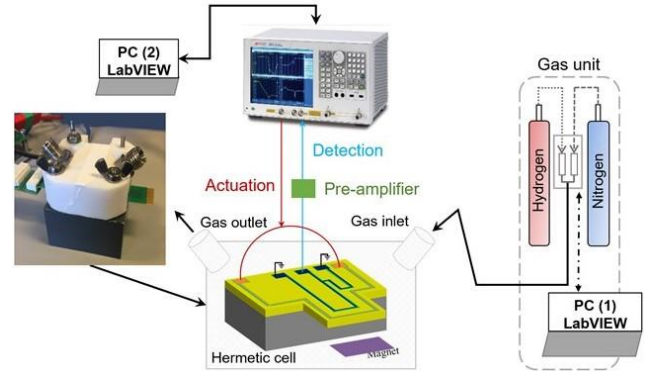


Fig. 4. Gas measurement protocol using 3C-SiC cantilevers.

In this study, the 3C-SiC cantilevers investigated are based on electromagnetic actuation and inductive detection. The circulation of a current in a track placed on the periphery of the cantilever, immersed in a magnetic field, leads to a Laplace force. Given the alternative nature of the current, it results in a vibration movement of the cantilever, impacted by the density of the surrounding gas. This vibration leads to an induced voltage on another conductive track. According to the results of [12], all the presented results of this study are based on the use of the linearization of the phase between the actuation voltage and the measurement of the induced voltage.

Results and Discussion

For all the experiments, hydrogen and carbon dioxide (CO_2) gases, diluted in nitrogen, have been investigated. Nitrogen has been used as its molar mass is very close to the one for air (28g/mol instead of 29g/mol). In this study, the proportion of the gas analysed was ranging from 0% to 2%, as presented in Fig. 5 where the change in resonance frequency of the cantilevers is presented as a function of the surrounding gas concentration. As highlighted, the change in resonant frequency is positive when the gas is lighter than N_2 , that is the case for H_2 , and negative when the gas is weightier, as observed with CO_2 . Moreover, the change in resonance frequency depends on the molar mass of the gas compared to the one of N_2 . It explains why the change in resonance frequency is around 3.3Hz for a H_2 concentration of 2% in N_2 whereas is limited to less than 2.5Hz for a CO_2 concentration of 2% in N_2 .

Detection of 0.2% for H_2 in N_2 and 0.25% for CO_2 in N_2 , have been achieved (Fig. 5), which can be considered as the limits of detection (LOD) for these two gases, using this SiC sensor. For hydrogen, this LOD is more than one order of magnitude lower than the lowest flammable concentration of this gas, evaluated to 4%, that illustrates the potential of these structures for security applications. And thanks to the physical properties of silicon carbide, these 3C-SiC-based MEMS devices could be operated in harsh environment, for example to detect H_2 release in the future underground facility dedicated to the storage of the long-life nuclear wastes, in France.

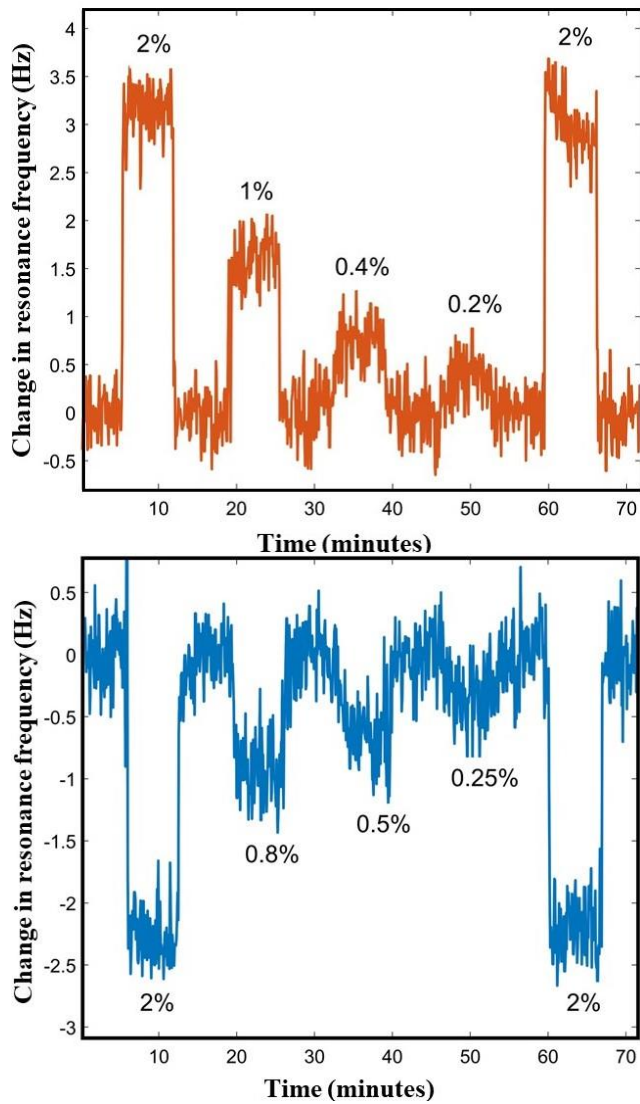


Fig. 5. Change in resonance frequency of 3C-SiC cantilevers, as a function of the surrounding gas concentration, for H₂ in N₂ (top) and CO₂ in N₂ (bottom). A limit of detection of 0.2% for H₂ and 0.25% for CO₂, in nitrogen, has been measured.

As already mentioned, gas sensing is mainly addressed using chemically functionalized or coated sensors, that can cause device failures like ageing, low reliability and high response time. In our case, due to the lack of sensitive layer, these concerns are circumvented, and our devices are perfectly suitable for binary gas mixture monitoring. But uncoated sensors selectivity is poor or non-existent, that could be a weakness of this technology to monitor environments composed of various gases. Fortunately, by measuring simultaneously several physical properties like both density and viscosity, it is possible to discriminate the gases and to determine their concentrations, using cantilevers.

Recently, our groups have also proposed another approach, based on capacitive micromachined ultrasonic transducers (cMUTs). These devices, usually exploited in the field of medical imaging, are composed of a suspended membrane, that can be actuated thanks to electrostatic forces. With membrane dimensions around 25 μm x 25 μm, the resonance frequencies are in the MHz range, that generates ultrasonic waves. But cMUTs can also be used to detect an acoustic wave. Therefore, these devices can be operated in emission and in reception. By combining these 2 modes, cMUTs can be exploited to perform time of flight (TOF) measurements. In this case, the propagation duration of the acoustic wave, from the emission to the reception, is governed by the gas acoustic property i.e., the ultrasound velocity. As highlighted in Fig 6, this TOF method allowed us to measure a concentration of H₂ and CO₂ in

nitrogen, of respectively 0.15% and 0.3%, which can be considered as the LOD of this sensor.

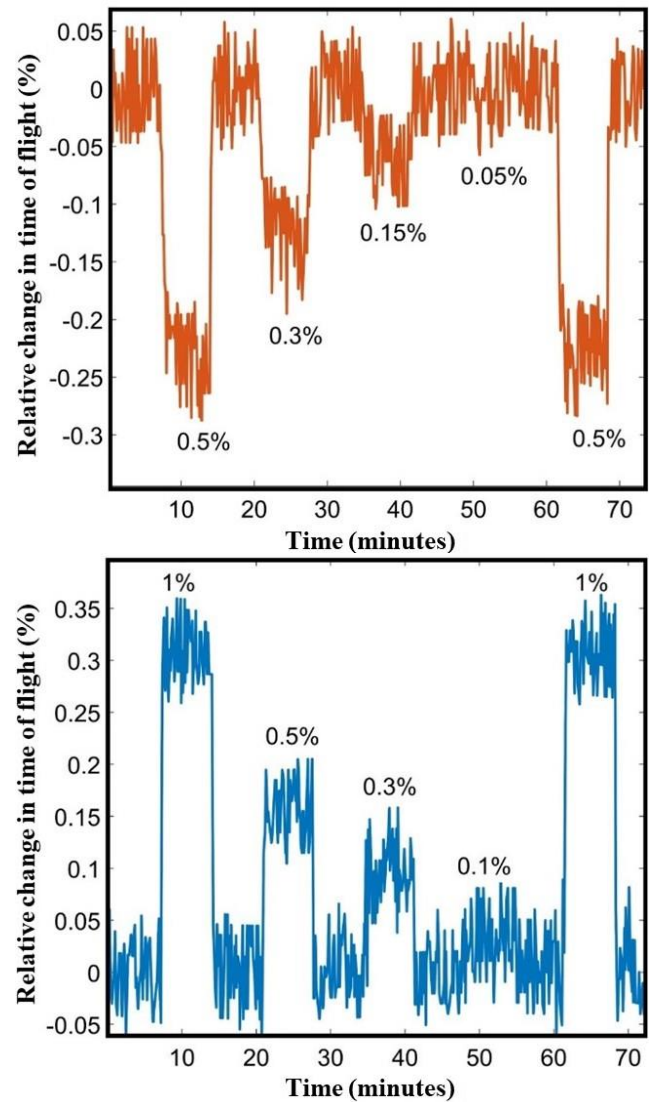


Fig. 6. Relative change in time of flight, using capacitive micromachined ultrasonic transducers, as a function of the surrounding gas concentration, for H₂ in N₂ (top) and CO₂ in N₂ (bottom). A limit of detection of 0.15% for H₂ and 0.30% for CO₂, in nitrogen, has been measured.

Due to changes in gas mass density, a shift in resonance frequency of the cMUTs can be also observed (not shown here). This second method led to a LOD of 0.04% for H₂ in N₂, that means two orders of magnitude lower than the lowest flammable concentration of this gas. Moreover, at lower frequencies than the resonance, face to face cMUTs can also be used to determine the attenuation coefficient of the gas environment. For this measure, a continuous ultrasonic sine wave is sent from the cMUTs emitter face to the cMUTs receiver face, after travelling the 5mm distance between the cMUTs arrays. The attenuation of the signal is linked to the gas environment between the 2 cMUTs faces.

By combining the 2 methods (TOF & attenuation), we demonstrated the opportunity to identify hydrogen, carbon dioxide and methane from each other, and to determine their concentrations [13]. Accordingly, cMUTs are another device that can be used to discriminate gases in their environment. Nevertheless, the cMUTs devices involved in this study were composed of a silicon nitride membrane, that is not a material perfectly adapted to harsh environments. To be able to use cMUTs in severe conditions, 3C-SiC would be more adapted. It will be the next step but, based on our preliminary results, we hope to succeed in the achievement of 3C-SiC-based cMUTs in the future [14].

Conclusions

In this contribution, we have presented uncoated 3C-SiC-based MEMS devices for gas detection. Limits of detection as low as 0.2% and 0.25% has been reached, respectively for H₂ and CO₂, in nitrogen.

Thanks to the physical properties of 3C-SiC, these devices will be operational in harsh environments, for example to detect hydrogen release in the future underground facility devoted to the storage of nuclear wastes. Actually, as this gas is flammable at a concentration of 4-70% in the volume of air, its continuous monitoring is mandatory. And due to the radioactive environment, the use of 3C-SiC-based sensors will be valuable.

Acknowledgments

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