In-Situ Grown Carbon Nanotubes for Enhanced CO_2 Detection in Non-Dispersive-Infra-Red System

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***Abstract* — Non-dispersive-infra-red (NDIR) sensors are believed to be one of the most selective and robust solutions for CO_2 detection, though cost prohibits their broader integration. In this paper we propose a commercially viable silicon-on-insulator (SOI) complementary metal-oxide (CMOS) micro-electro-mechanical (MEMS) technology for an IR thermal emitter. For the first time, vertically aligned multi walled carbon nanotubes (VA-MWCNTs) are suggested as a possible coating for the enhancement of the emission intensity of the optical source of a NDIR system. VA-MWCNTs have been grown *in situ* by chemical vapour deposition (CVD) exclusively on the heater area. Optical microscopy, scanning electron microscopy and Raman spectroscopy have been used to verify the quality of the VA-MWCNTs growth. The CNT-coated emitter demonstrated an increased response to CO_2 of approx. 60%. Furthermore, we show that the VA-MWCNTs are stable up to temperatures of 500 °C for up to 100 hours.**

I. INTRODUCTION

The demand for low-cost, high selectivity, low power and long life-time gas sensors has significantly increased over the past decade owing to the ubiquity and reduced cost of portable electronic devices. To date, electrochemical, catalytic and metal oxide gas sensors dominate the low-cost gas sensing market. However, electrochemical sensors suffer from short life-times [1], whilst poisoning [2, 3] and high power consumption [4] are key drawbacks of catalytic and metal-oxide technologies. In addition, temperature drift, poor long-term stability and very poor reproducibility of the metal oxide resistive sensors are still issues to be addressed in spite of their low cost and enhanced sensitivity. Non-dispersive infra-red (NDIR) spectroscopic gas sensors are expensive [5], largely due to system complexity, but offer high accuracy, high reliability and enhanced selectivity [1]. Recently, much effort has been dedicated towards the development of low-cost, ultra-miniaturised NDIR systems [6], driven by a burgeoning number of applications. Exploiting standard CMOS processes is an attractive route toward the fabrication of such infrared emitters and detectors. Yet, the emissive and absorptive properties of these devices often need to be modified to fulfill particular application requirements – such as gas selectivity. Several solutions have been proposed including "black" coatings [7], and quarter-wavelength structures [8], in addition to plasmonic [9] and photonic crystal structures [10]. However, these solutions are often CMOS incompatible.

Yang *et al.* [11] demonstrated that a low density vertically aligned nanotube array based material can be engineered to allow the creation of an extremely low reflectance object. However, their experiments, based on the theoretical predictions by García-Vidal *et al.* [12], were limited to the visible spectrum. Mizuno *et al.* [13] found that "forests" of vertically aligned single-wall carbon nanotubes have remarkably high emissivity, which was nearly wavelength independent between 5 μm and 12 μm. The application oriented work of Lehman *et al.* [14, 15] showed that vertically aligned multi-walled carbon nanotubes could increase the sensitivity of a pyroelectric detector in the IR (up to 15 μm).

In the past, we have demonstrated local growth, on micro-hotplate platforms, of both spaghetti-like and vertically aligned single-walled and multi-walled carbon nanotubes [16]. In all cases the CNTs were grown by CVD exclusively on the heater area (*in-situ* growth) of SOI-CMOS microhotplate based micro-reactors. We have also shown the feasibility of wafer level *in-situ* growth [17], where we performed simultaneous growth on many hundreds of sub-millimeter reactors, which we believe afford one route toward the mass production of novel CNT-based devices.

In this paper, for the first time, we report on the *in-situ* growth of VA-MWCNTs on SOI CMOS-compatible microhotplate based IR thermal emitters for emissivity enhancement to improve their CO_2 sensitivity in a miniaturised NDIR system.

II. OPTICAL SOURCE DESIGN AND FABRICATION

The IR emitter was designed using the standard Cadence™ Virtuoso® custom design platform. A schematic cross-section and a photograph of the actual device are shown in **Fig. 1** and **Fig. 2**, respectively. The emitter chip features a 300 μm diameter tungsten micro-heater embedded in a 600 μm diameter dielectric membrane. Accurate emitter temperature

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control is enabled by the Si p+/n+ diode temperature sensor placed underneath the micro-heater. Tungsten was chosen as the heating element and interconnection metal due to both its superior resistance toward electromigration and high glass transition temperature - in comparison with doped poly-silicon or aluminum. Thermal emitters were fabricated using a 6" wafer SOI CMOS process in a commercial foundry. The circular membrane was obtained with a deep reactive ion etch (DRIE) of the backside, post-CMOS MEMS process, in the same foundry. During this latter process the buried SiO_2 layer functioned as an etch-stop. The silicon dioxide membrane is approx. 5 µm thick, for effective thermal isolation without compromising device robustness, and features nearly vertical side-walls, allowing aggressive miniaturisation. The wafers were laser diced into 1 mm^2 dies in a commercial dicing house, and subsequently packaged in house in standard TO5 packages using a gold wire wedge bonder.

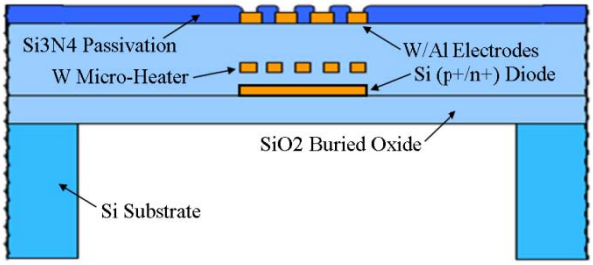

Fig. 1: SOI-CMOS MEMS technology cross-section (not to scale).

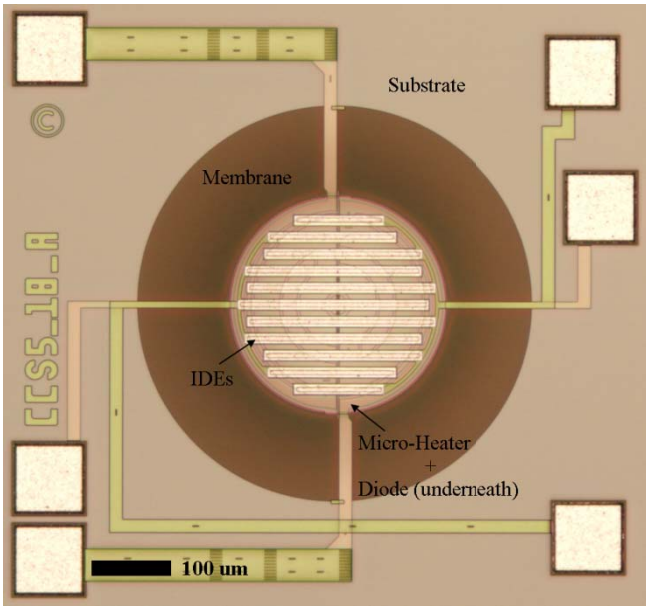

Fig. 2: Optical micrograph of an SOI CMOS-compatible IR thermal emitter, featuring a 300 µm diameter heater embedded in a 600 µm diameter dielectric membrane. Die size 1 mm × 1 mm,

III. CNT Growth and Characterization

Thermal chemical vapour deposition (T-CVD) is a common technique for CNT growth. In standard T-CVD processes, substrates are first coated with a metal catalyst, often Fe, Ni, Co, then heated to > 500 °C to obtain nm-scale islands. When a carbon feedstock (such as CO, C_2H_2, CH_4, etc.) is added the catalyst mediates thermal decomposition of the source and becomes supersaturated with carbon. CNTs are then extruded from this carbon reservoir within the catalyst. Unfortunately, because of the high temperatures, which damage the CMOS circuitry, this process is not CMOS compatible. Our micro-hotplates are capable of reaching temperatures in excess of 750 °C in a localized "hot zone", without compromising the functionalities of the peripheral CMOS circuitry placed on the chip substrate, due to the thermal isolation offered by the thin dielectric membrane. Hence, such micro hotplates can be effectively employed as CMOS compatible micro-reactors, and allow viable CNTs-CMOS integration at the wafer level.

Herein, VA-MWCNTs were grown at 25 mbar from a bilayer catalyst Al/Fe (10/1 nm) in a 4% H_2:C_2H_2 atmosphere at 700 °C for 10 min. Micro hotplates were powered with a LabView controlled Keithley 2401 source meter. For accurate temperature control a temperature feedback control was implemented at the software level. It is worth mentioning that even though the emitters are characterized by very fast thermal transient times (~ 10^4 °C/s), the heating and cooling thermal ramp rates were slowed down to 10 °C/s to minimize thermal stress on the membrane.

CNT growth was verified by optical microscopy and scanning electron microscopy (SEM). In **Fig. 3a-b** optical photographs of IR emitters before (a) and after (b) growth are presented, where the CNT forest is clearly observed on the hot zone.

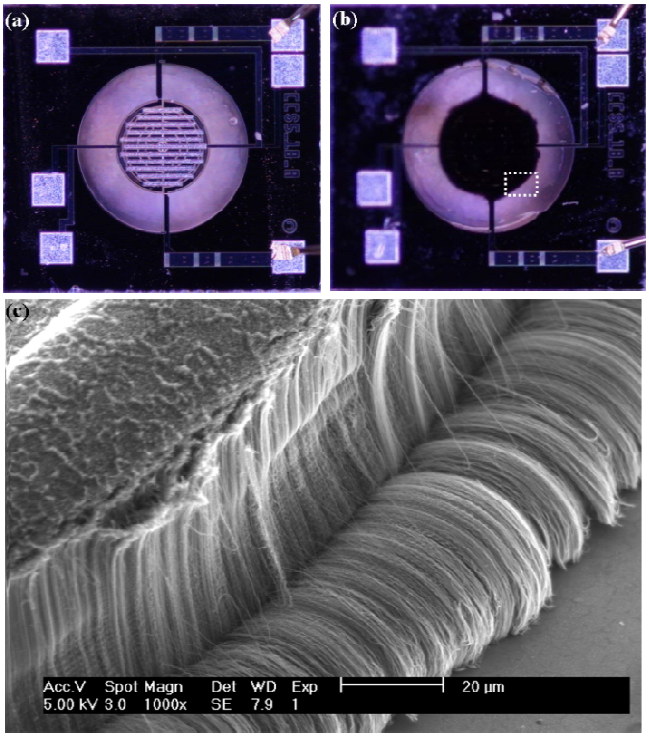

Fig. 3: (a) Optical photograph of a bare IR emitter before *in-situ* growth, (b) Optical photograph of a coated IR emitter after *in-situ* growth, (c) Scanning electron micrograph of *in-situ* grown VA-MWCNTs at the edge of the heater (dotted area in b).

SEM imaging confirmed the successful growth of VA-MWCNTs. In **Fig. 3c** CNTs at the edge of the heater area are shown. The MWCNTs were 25 nm in diameter with 2-5 graphitic sidewalls. Raman spectroscopy (457 nm), shown in **Fig. 4**, is consistent with values reported for MWCNTs and shows an ID/IG ~ 0.45 and an IG'/IG ~ 0.66.

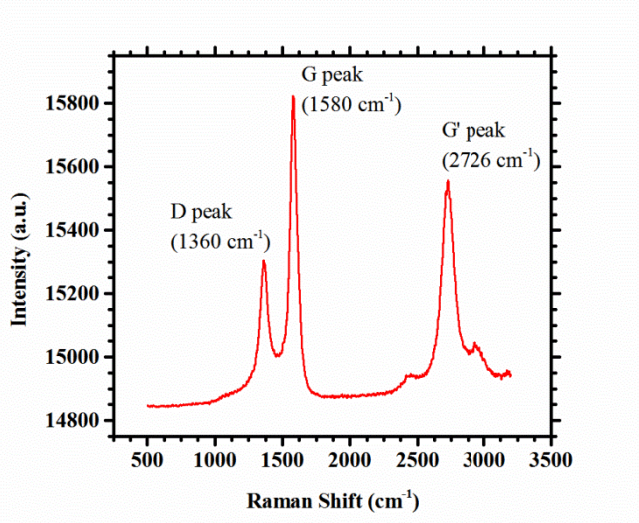

Fig. 4: Raman spectrum of VA-MWCNTs under 457 nm excitation.

IV. Results and Discussion

NDIR spectroscopy is based on the principle that each molecule absorbs IR radiation at a specific wavelength which is representative of a vibrational energy of the molecular bond; in the case of CO_2 the main band is centered at 4.26 µm. A NDIR system relies on an IR optical source to generate thermal radiation, which is partially absorbed by the target gas given by the Beer-Lambert law. The unwanted transmitted radiation is optically filtered and the remainder is detected by an IR detector (typically a thermopile or pyrodetector). The detector output can be then correlated to the gas concentration *via* a calibration procedure. IR emitters are electro-thermo-optical transducers. They are electrically stimulated to deliver an optical output *via* heat. Electrical power is converted into thermal power, with the latter then being converted into optical power. This double transduction is performed *via* Joule heating in a metallic or semiconductor resistor (in our case tungsten), where the thermal output is partially dissipated through the membrane by conduction, and partially through the ambient *via* convection. The remainder accounts for the functional and measureable optical component *via* radiation. To enhance the ratio between the useful radiative power versus the wasted power, operation at the highest possible temperature is required. An IR detector performs the transduction in the opposite direction. The surface of the detector is thermally excited by the incident radiation with the thermopile converting the temperature into a proportional voltage.

The electro-thermal efficiency is strongly dependent on the emitter design. The ratio between heater and membrane diameter is of prime importance. For a given heater diameter, the larger the membrane diameter the lower the power dissipation, due to the improved thermal isolation. In **Fig. 5** power as a function of emitter temperature is presented. The extrapolated efficiency is approx. 0.15 mW/°C, resulting in around 75 mW DC power dissipation at a constant working temperature of 500 °C. Such low power consumption is very attractive for portable (battery powered) applications.

Nevertheless, the high heater temperature does not guarantee high optical power output in the CO_2 absorption region, as predicted by Planck's equation. We have theoretically shown and experimentally observed that the thermo-optical efficiency, or emissivity, of our emitters is poor for wavelength lower than 7 µm [18]. Herein, we employ *in-situ* grown VA-MWCNTs, which have high wavelength-independent emissivity, to enhance the thermo-optical efficiency of our IR emitters. Such improvement was assessed by comparing the voltage output of a commercial high sensitivity thermopile (TPD1T0515, Excelitas) to a CNT-coated and an uncoated IR emitter in the presence of 100% zero air or 100% CO_2. The emitter and the detector were placed in a 16 mm diameter cylindrical chamber ~7 cm apart and the gases were introduced using digital mass flow controllers (MC-5SLPM-D/5M, Alicat). As shown in **Fig. 6**, the CNTs-coated emitter generated an approx. 60% larger change in response relative to the uncoated emitter, at a working temperature of 500 °C. The response transient time (about 8 s) is not due to the optical source or detector, but it is limited by the chamber filling time.

When operated at high temperature carbon based materials burn-off in presence of air. However, in **Fig. 7** we show, rather surprisingly, that for temperatures up to 500 °C, the detector output is very stable over a 100 hour continuous DC test. The drift in the sensor output is about 1.3 %.

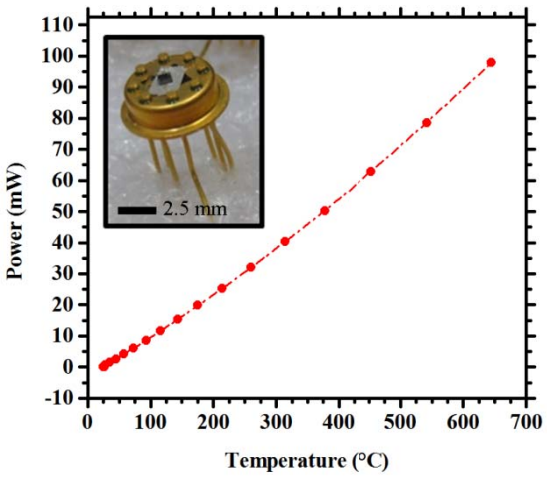

Fig. 5: Power vs. Temperature plot of the IR optical source. *Inset:* optical photograph of IR emitter wire bonded to a standard TO5 package.

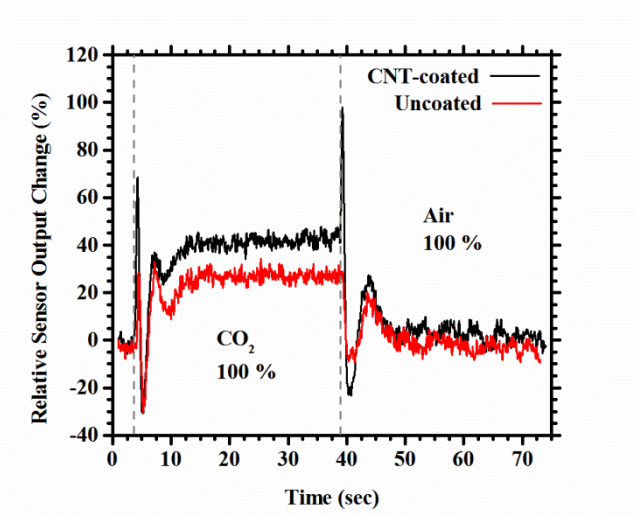

Fig. 6: Normalised time dependent NDIR detector output for CNT-coated and uncoated IR optical sources during CO_2/Air pulsing.

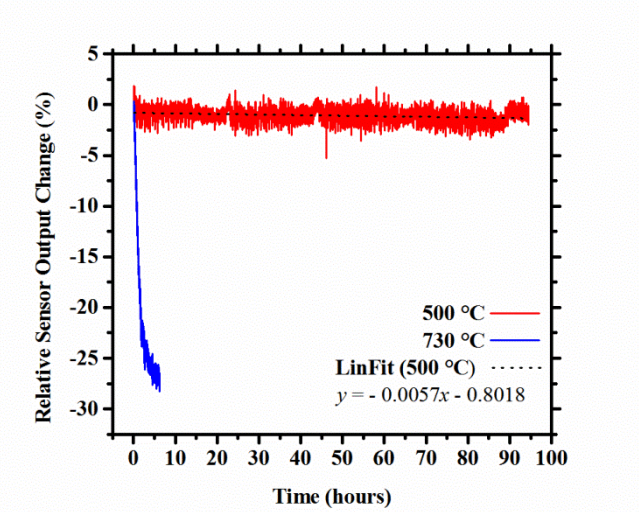

Fig. 7: Change in detector output as a function of time, for CNT coated optical sources working at 500 °C and 730 °C. Linear fit of the detector output change for the emitter working at 500 °C is superimposed for clarity.

V. Conclusion

We have reported on the *in-situ* growth of VA-MWCNTs on SOI CMOS-compatible microhotplate based IR optical sources as an effective additive for emissivity enhancement which we employ to improve CO_2 sensitivity in a miniaturised NDIR system. We have shown that our emitters can operate at high temperature with limited power dissipation, due to their small size and excellent thermal isolation. An approximate improvement of 60 % in CO_2 detection and excellent thermal stability (drift < 1.3 %) for 100 hours have been demonstrated.

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