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Low-power, Chip-Scale, CO_2 Gas Sensors for Spacesuit Monitoring

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N5 Sensors, Inc. and NASA through a STTR program are jointly developing ultra-small, low-power carbon dioxide (CO_2) gas sensors, suited for monitoring CO_2 levels inside the spacesuits. Due to the unique environmental conditions within the spacesuits, such as high humidity, large temperature and operating pressure swings, measurement of key gases relevant to astronaut's safety and health such as carbon dioxide, is quite challenging. Conventional non-dispersive infrared absorption based CO_2 sensors cannot be effectively implemented inside the spacesuits due to their sizes, weights, and power constraints. Metal-oxide based sensors have been effectively miniaturized for several applications, however detection of CO_2 utilizing metal-oxide based sensors is challenging due to the chemical inertness and high stability of CO_2 at room-temperatures. To mitigate these limitations, unique chip-scale, nanoengineered chemiresistive gas-sensing architecture has been developed - to allow the Metal-oxide sensors to operate in space-suite environmental conditions. Unique design combining the selective adsorption properties of the nanophotocatalytic clusters of metal-oxides and metals, provides selective detection of CO_2 in high relative humidity conditions. All electronic design provides a compact and low-power solution, which can be implemented for multipoint detection of CO_2 inside the spacesuits. This paper will describe a novel approach in refining the sensor architecture, development of new photocatalytic material for better sensor performance.

Nomenclature

AFM = Atomic force microscope
NDIR = Non-dispersive infrared
CO_2 = Carbon dioxide
GaN = Gallium nitride
ISS = International space station
LED = Light emitting diode
PLSS = Portable life support system
SnO_2 = Tin oxide
TiO_2 = Titanium oxide
UV = Ultra violet
RF = Radio Frequency
XPS = X-ray photoelectron spectroscopy

Introduction

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The Extravehicular Mobility Unit (EMU) is an independent anthropomorphic spacesuit which is used by astronauts to perform elaborate and dynamic tasks in harsh spacial conditions. One key part of EMU is the Primary Life Support System (PLSS), which is used to provide breathable oxygen and remove carbon dioxide, humidity, odors, and contaminants from the breathing oxygen. Typically, a collection of sensors is used to monitor the proper operation of the PLSS and ensure the safety of astronauts and allow them to safely accomplish their missions. The low pressure (4.3 psi) and 100% oxygen atmosphere of the EUVs and the common occurrence of water condensation present unique environmental conditions unlikely to be encountered on Earth, a pressurized crewed space vehicle, or a planetary base and therefore require uncommon considerations and specialized testing.

Monitoring the CO_2 concentration is critical to the PLSS and EMU operations. Presently, infrared gas transducer is commonly used in the EMUs to measure and report the concentration of CO_2 in the ventilation loop. The optical method for gas sensing is expensive and its maintenance is difficult. The next generation of the PLSS requires next generation CO_2 sensing technology with performance beyond what is presently in use on the Space Shuttle/International Space Station EMU.

Metal oxide is a mature material widely used in gas sensing industry where small-form factor is desired. However, there are several limitations of metal-oxide sensorsincluding high operation temperature , which is due to the stability of surface adsorbed oxygen and hydroxyl radicals at room temperature. The consequence of high operation temperature requirement is correlated to a large power consumption related to the micro-heater integrated in the gas sensor design. To overcome this challenge, the engineered nanocluster layer works through dynamic active sites generation at the surface. The photo-desorption of adsorbed oxygen and hydroxyl radicals is utilized to improve the performance, thus reducing the operation temperature.[1] This results in low power consumption and long-term stability. This work reports the development of low-power, single-chip based CO_2 sensors through GaN nanowire decorated with nanocluster layer. Benefiting from the photocatalytic sensing, those sensors show good response at room temperature and improvement of system reliability. They are also microgravity-compatible with radiation-tolerance due to GaN large bandgap and thin nanocluster layer. These characteristics of the developed sensors make them deployable for harsh space environments.

Optically enabled chemi-resistive sensing

The proposed gas sensor emulates the behavior of a resistor, which is subject to change when exposed to the target gas. The commonly accepted redox and semiconductor bandgap theories can be applied to explain our gas sensor operation.[2] The target gas interacts with the surface of the metal oxide film, which results in a change in charge carrier concentration of the material. This change of charge carrier concentration can be detected through measuring the conductivity (or resistivity) of the material. The working principle of n-type material is shown in Figure 1. Oxygen molecules are pre-adsorbed at the surface of the n-type oxide semiconductors by taking electrons near the surfaces of the semiconductors, which leads to the surface depletion and surface band bending. When the gas sensor is exposed to the reducing gases, those ionized oxygen anions tend to oxidize the reducing gases, and inject electrons into the semiconductor material. This process reduces the surface depletion region and increase the conductivity. On the contrary, if the sensor is exposed to oxidizing gases, the surface depletion region increases and conductivity of gas sensor decreases.

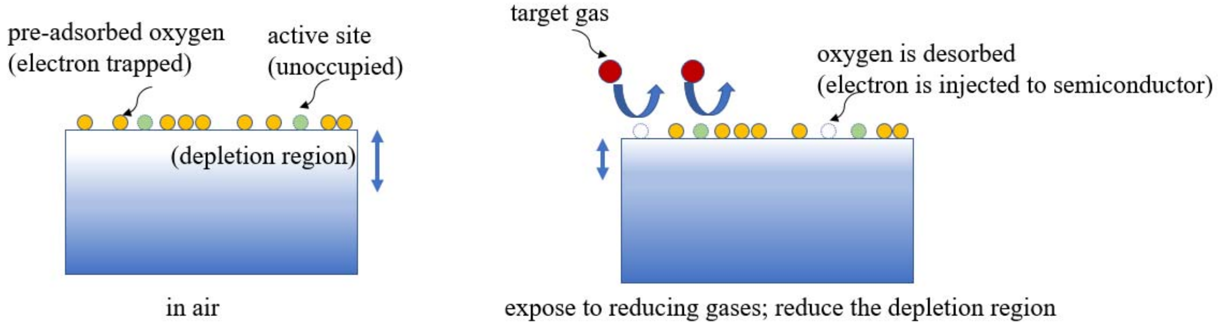


Figure 1. Schematic of operation principle of chemi-resistive device

To improve the surface reactivity, most metal oxide gas sensors prefer high operation temperature, which leads to large power consumption. Dynamic active sites generation via UV desorption from surface sites is utilized in the proposed gas sensor to reduce the operation temperature. As shown in Figure 2, those pre-adsorbed oxygens are stable at room temperature without UV illumination. The absence of generated output signal during CO_2 exposure is due to an insufficient number of active sites for CO_2 adsorption and electron transfer. However, if the device is exposed to UV illumination, those stable oxygens are dynamically desorpted through photo-desorption. Enough active sites will be generated for CO_2 sensing.

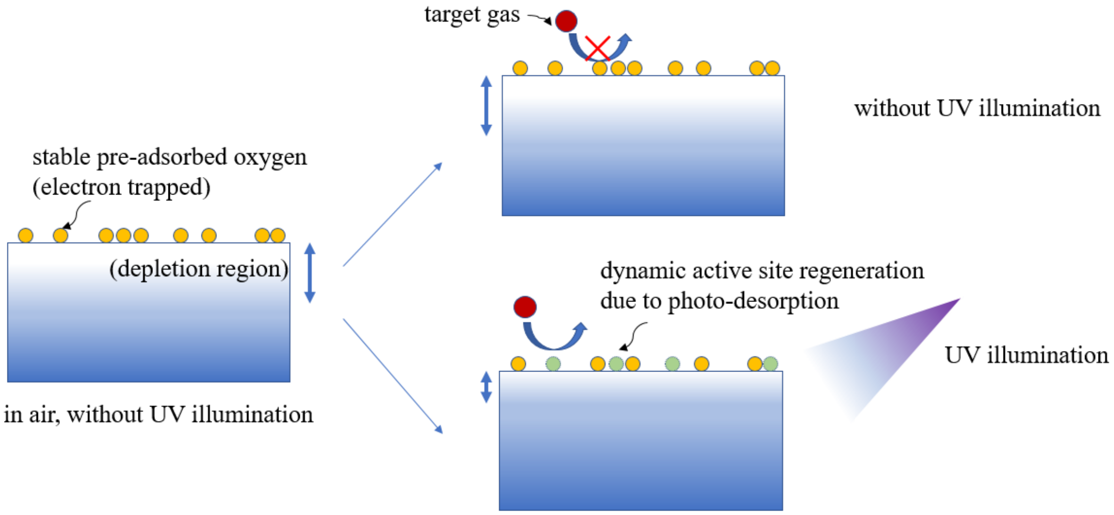


Figure 2. Schematic of dynamic active sites generation

Sensor Architecture and Design

The proposed sensor is composed of two components: the receptor and the transducer. Figure 3 shows the schematic of the gas sensor structure which compromise the transducer, the receptor, and nanocluster layer. The transducer is a two terminal GaN nanowire backbone.[3] The receptor functionality is provided by the unique surface functionalization layer consisting of a nanoscale photocatalytic metal-oxide and /or metal coating. The nanocluster layer only covers part of the nanowire and doesn't touch the contacts. There is no conduction through the nanocluster layer. Under the UV illumination, photo-induced charge carriers are generated both in the transducer and receptor materials. The photocurrent is modified by the adsorption of target gases on the surface functionalization layer, and thus be detected.

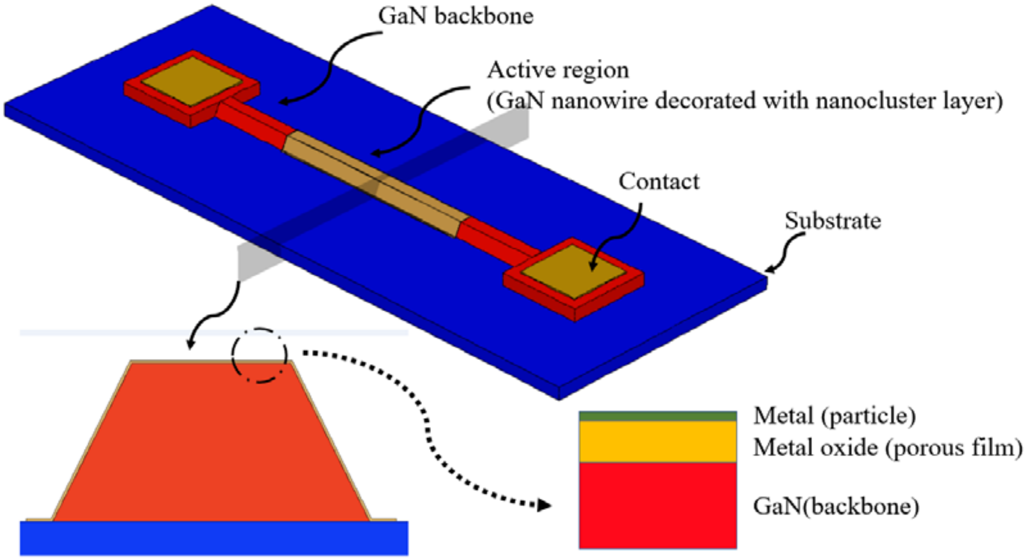


Figure 3. Schematic of sensor architecture (not drawn to scale)

The doping concentration and dimension of the GaN are optimized to get high response and large signal-noise ratio(SNR). Figure 4 depicts the effect of GaN depletion width variation on electron concentration, n_e, normalized to the doping concentration, N_d, . Lower doping concentration brings larger depletion width, and thus higher response. However, extreme high resistance will make the device measurement difficult and more sensitive to the process variation. There is a complicated trade-off between the gas sensing response and device stability. Similar problem will be faced when choosing the dimension of the GaN nanowire.

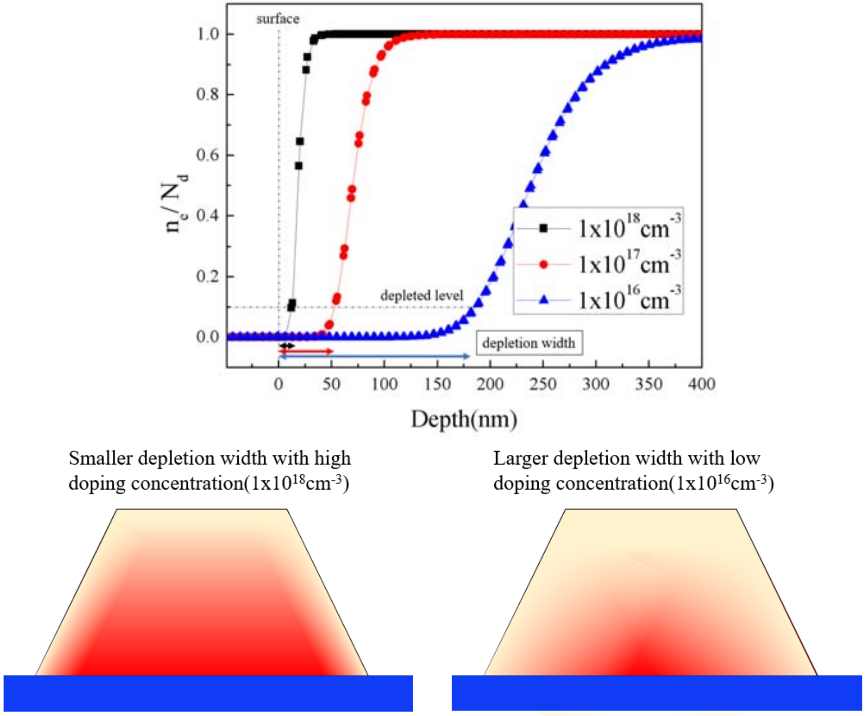


Figure 4. Effect of GaN backbond doping to the surface depletion width: a) carrier concentration distribution near the surface due to depletion; b) schematic of different surface depletion

From the perspective of target receptor, sensing of CO_2 is challenging, considering the difficulty of activation and splitting of CO_2 molecule on an oxide surface at room temperature. As CO_2 is nonpolar and has two double bonds, its activation requires high temperature/pressure conditions and/or active reductants, such as hydrogen. It makes choosing proper metal oxide more difficult.

It is a well known fact that chemisorption of CO_2 at oxide surfaces is a complex process, involving adsorption and formation of stable carbonate species on different oxides. If we consider the adsorption energy profile on various transition oxides to make the adsorption process happen, one can find that the adsorption energies for CO_2 are much higher on basic oxides such as MgO, CaO, ZnO. However, all these reactions are slow at room temperature. Hence, we prefer to choose other materials which can offer rapid room-temperature operation.

Another key part is the electron transfer process and the formation of stable carbonate species. It is important to activate CO_2 under ambient conditions with the help of a solid-state catalyst. The role of catalyst is to adsorb CO_2 molecules and facilitate electron transfer to them. Alkaline earth metals and alkaline earth metal oxides are the mostly investigated materials to form the 'bent' $CO_2^{\delta-}$ configurations. But it should be noticed that only the formation of $CO_2^{\delta-}$ does not lead to the detectable signal. A preferred option is to utilize surfaces of transition and sp metals (like Cu) to activate CO_2 and generate CO through decomposition of $CO_2^{\delta-}$ and/or $CO_3^{\delta-}$ intermediates. [4]

Based on the difficulty of CO_2 sensing, we proposed the two components functionalization layer with one primary metal oxide and a secondary metal component. Amphoteric oxides such as TiO_2 and SnO_2 are good choices as a primary oxide. For the choice of the seondary component, Cu is used based on the acid strength factor. Also, adsorption of CO_2 on CuO surface is favorable under ambient condition from thermodynamics considerations.

The thickness of metal oxide is one of the key parameters that needs to be optimized. By modelling the device, we calculated the optimal thickness of the metal oxide (about 4-6 nm), which is the maximum of the curve as shown in Figure 5.

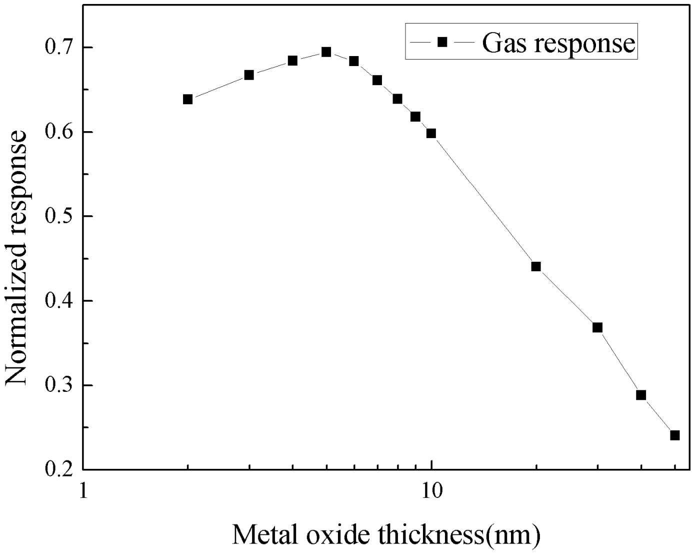


Figure 5. The effect of metal oxide thickness to the gas sensing response

Device fabrication

The sensor fabrication mainly includes two parts: 1)fabrication of the sensor backbone (GaN nanowire) and 2) fabrication of the receptor layer (metal oxide and metal particles).

The GaN wafer was purchased from EpiGaN. After standard cleaning procedures, hard mask by depositing patterned metal was used for protecting the defined GaN nanowire during ICP etching. Then metal stack of Ti/Al/Ti/Au was deposited to form Ohmic contacts. Fully covered SiO_2 was deposited thereafter to improve the yield and stability of the sensor.

The functional receptor, which selectively adsorbs the target analytes, is comprised of metal oxide thin film (its thickness is smaller than 10nm typically) and metal nanoparticles(diameter less than 5nm). They were deposited through the window of active region. Before the functional receptor deposition, top SiO_2 layer was etched in this window to make sure functional receptor layer is directly covering on the GaN nanowire surface. The primary metal oxide thin film was deposited through a RF magnetron sputtering tool. The sputtering was conducted in reactive atmosphere with O_2 flow. The secondary functional metal particles were deposited through Ebeam evaporation. The thickness, porosity, phase and stoichiometry of functional receptor have significant effect on the sensitivity of the final sensor. So the deposition process and annealing optimization are critical. However, it should be acknowledged that due to the complex nature of the mechanisms involved at the surface of these clusters, it is difficult to predict the effect of all there parameters, without signification experimentation and rapid iterations.

After the functional receptor deposition and annealing, metal stack of Ti/Au was deposited in Ebeam evaporation to form the bonding pad. Finally, wafers were diced and packaged with chip carrier.

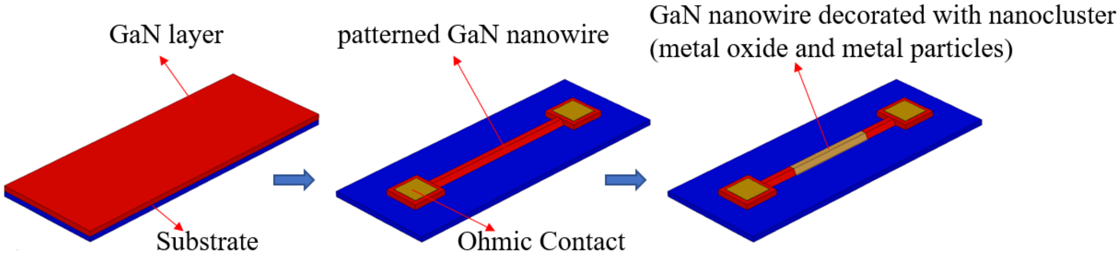


Figure 6. The main steps of sensor fabrication.

Figure 6 shows the main steps of sensor fabrication (passivation layer of SiO2 is not shown). The image of the full chip (without bonding pad) has been shown in Figure 7. There are totally 8 nanowires in each chip.

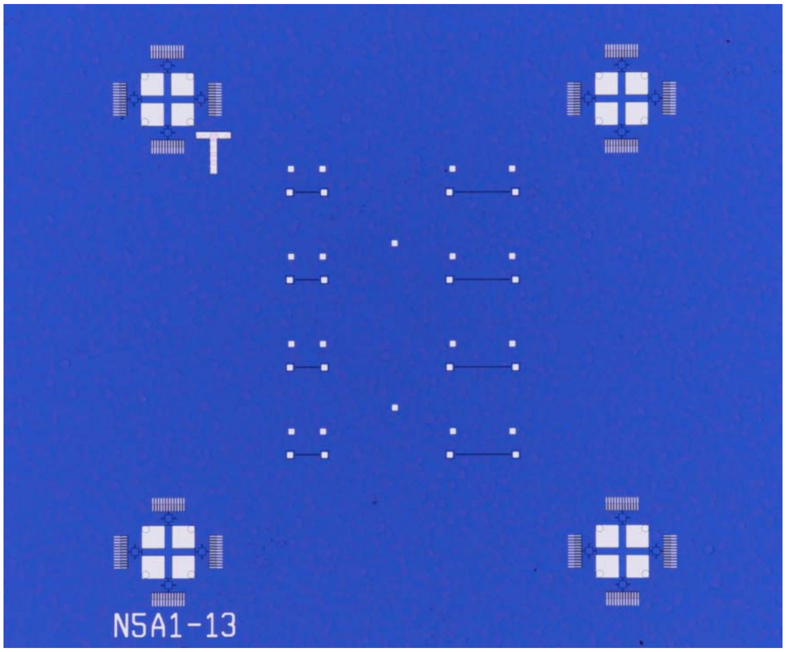


Figure7. Image of sensor chip in microscope

Sensor Module Design

As described above, the gas adsorption happens mainly on the functional nanocluster layer which is comprised of metal oxide thin film and metal particles. At the same time, we integrated a passivated GaN nanowire which was covered by SiO_2. The passivated nanowire will work as a reference device with a constant resistance when it is exposed to any analytic target gases.

The reference nanowire is designed to calibrate the active nanowire, offer a conductance baseline. More importantly, it helps to transfer the conductance change of the real detector to a voltage signal in a voltage divider circuit, as shown in Figure 8(a). The voltage signal output is beneficial to the back-end signal processing. Also, a good reference nanowire design is important to the bridge circuit design, which can help decreasing the noise, as shown in Figure 8(b). To make the resistance of reference nanowire close to the resistance of active detector, detailed analyzing has been done and the length modulation factor f (f equals to the ratio of reference nanowire length to the active nanowire length, to match their resistance) has been calculated and applied to our sensor module design. Table 1 shows the typical values for different metal oxides.

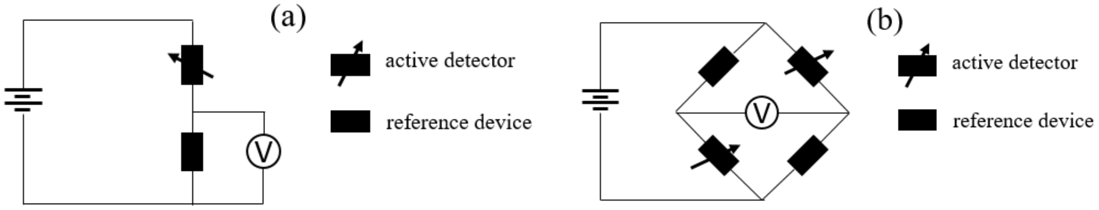


Figure 8. Voltage divider circuit(a) and Bridge circuit(b).

Table 1. The typical value of length modulation factor *f* for different metal oxides.

Metal oxide	*f*
SnO_2	1.6
ZnO	1.25
TiO_2	2
NiO	1.25

In section II, we discussed the importance of UV illumination to the gas sensor performance. In our sensor module, to improve the gas sensing response, an UV LED chip (peak wavelength is 310nm) is integrated with the gas sensor chip in the same chip carrier. A polished metal lid with a small hole (for gas exposure) is covered on the top of the chips(sensor chip and LED chip) to make the sensor chip immersed in the UV illumination, as shown in Figure 9.

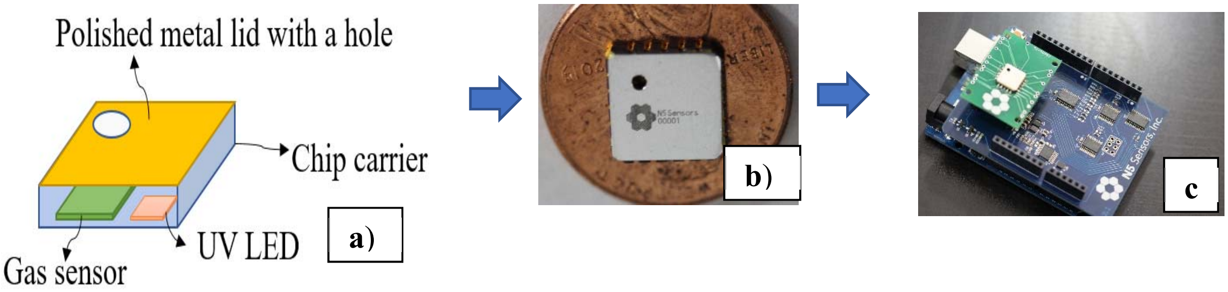


Figure 9. Sensor Integration Process gas sensor and UV LED :a) Drawing; b) LCC package; c) module.

Sensor Test and Performance Evaluation

The fabrication reliability and reproductibility are important to the mass production. We conduced process variability studies over the 4-inch wafer through the data aggregation. As shown in Figure 10, the passivated devices over the whole wafer have been analyzed. We can see that the uniformity of the contact performance and nanowire dimension is controlled well in our fabrication process.

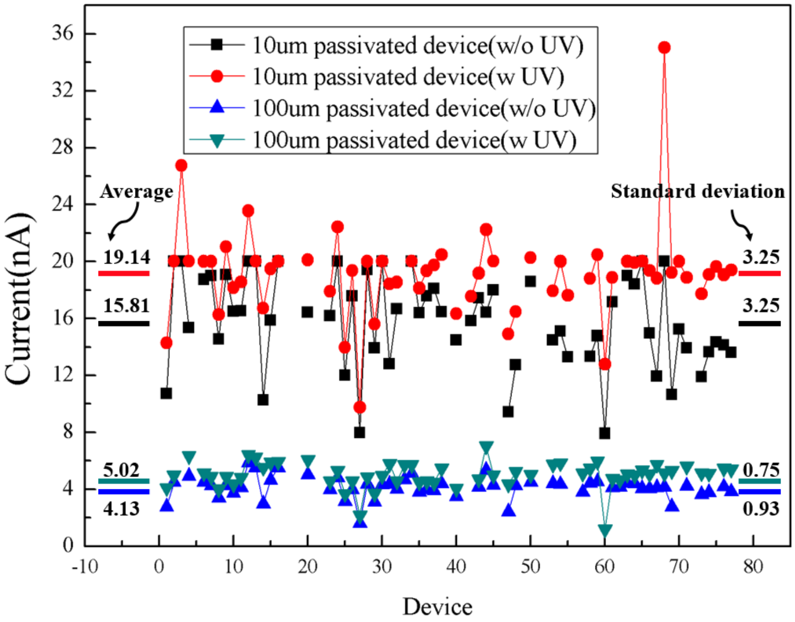
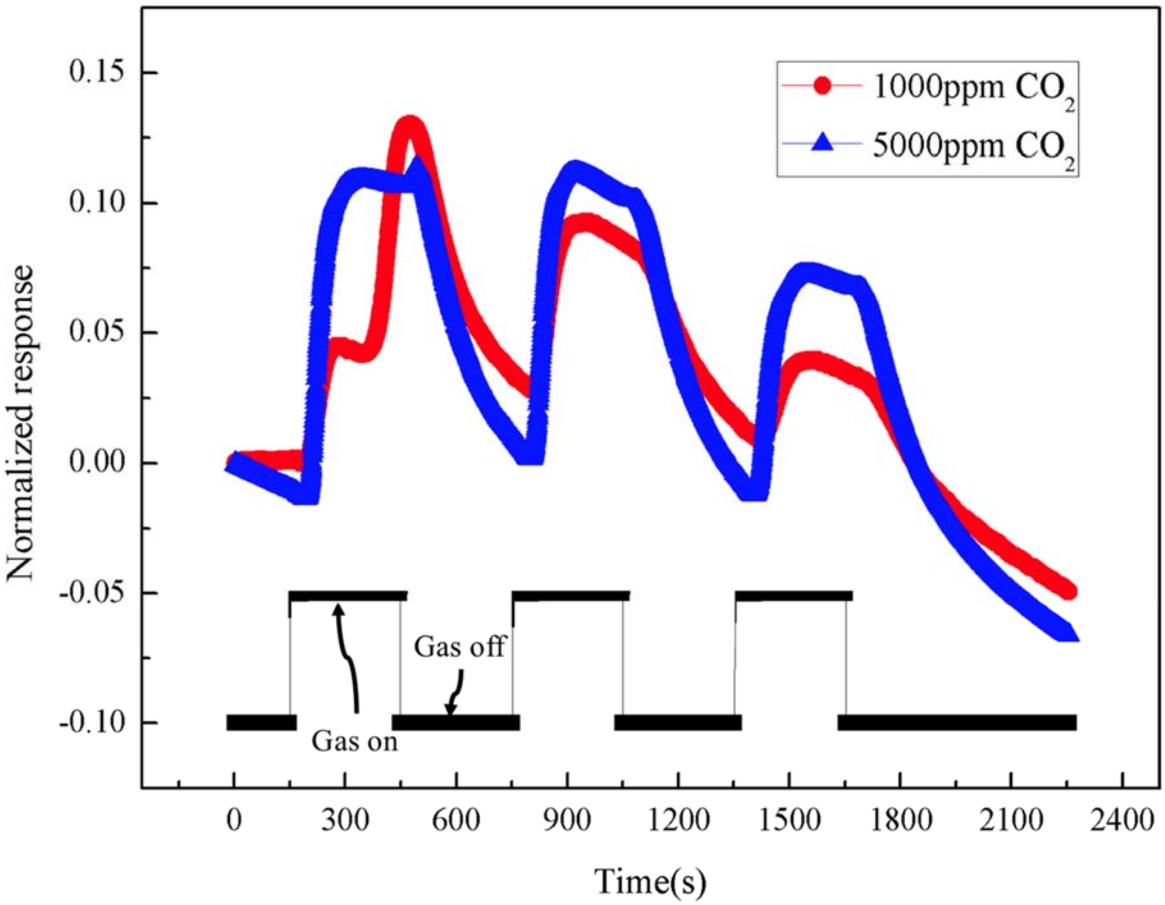


Figure 10. Analyzing of the current of passivated devices from the whole wafer

CO_2 gas sensing test has been shown in Figure 13. 1000ppm and 5000ppm CO_2 sensing performances have been illustrateded. After exposure to CO_2, the sensor resistance decrease. About 10% response has been observed for 5000ppm CO_2 exposure. About 5% response has been observed for 1000ppm CO_2 exposure. It shows fast response (response time is about 100s) and relatively slow recovery (recovery time is larger than 300s).



Conclusion and future advancement in design and performance

N5 Sensors has developed a novel CO_2 sensing device based on GaN nanowire decorated with functional nanocluster layer. The dynamic active site generation through photo-desoprtion makes CO_2 sensing at room temperature possible. Sensor devices have been optimized through theoretical calculations and experiments. The control and reliability of fabrication process has been analyzed for large volume fabrication Using standard semiconductor manufacturing processes. The recorded sensor response display metric of performance suitable for room temperature and high humidity conditions. The gas sensing performance and low cost, chip scale make the proposed detector a potential candidate sensor in the next generation PLSS.

Future work will focus on the further optimization of the sensor design. From a material perspective, metal oxide deposition, annealing, functional metal particle deposition can be further optimized. Future research can be also expanded to the metal oxide plus another metal oxide (for example, SnO_2 decorated with WO_3 particle). New materials (Gd_2O_3, La_2O_3 et al.) which are potential for CO_2 gas sensing can be also investigated. From a device structure perspective, Kelvin structure will be utilized to effectively eliminate the negative effect from the contacts. Sensors with different function metal oxide integrated in a single chip can be explored to further improve the sensitivity and selectivity.

Acknowledgements

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