Project title:
Design and Fabrication of Ultra-Low-Power Gas Sensors

Team Members:
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Statement of Project Goals:
The overarching goal of this project is to develop ultra-low power self-heated gas sensors for use in the Health and Environmental Testbed platforms. In year 3, the specific objective is 1) to fabricate low power (< 1mW) metal oxide nanowire gas sensors using atomic layer deposition (ALD) technique, 2) to develop GaN based semiconductor gas sensors, and 3) to evaluate the effect of surface functionalization in order to enhance the ability to detect very low concentrations, and 4) to deliver a packaged sensor for use in the ASSIST testbeds group.

Project’s Role in Support of the Strategic Plan:
The goals of the ASSIST are 1) to advance solutions in energy harvesting for enabling self-power operation, 2) to reduce power consumption of non-invasive nanoenabled sensors for reliable and wearable health/environmental monitoring, 3) to design and demonstrate ultra-low power system on chip, and 4) to demonstrate wearable, flexible, and biocompatible system. The main goal of this project is to develop ultra-low power, non-invasive, and reliable gas sensors that are essential component in the ASSIST wearable system for the Health and Environmental Tracker testbed. Therefore, this project is a core project that directly supports the goal of the ASSIST. In the ASSIST center, this project directly feed into the Thrust III, Wearable Nano-sensors, for the Gen 1 and 2 ASSIST Health and Environmental Tracking (HET) testbeds.

Discussion of Fundamental Research, Educational, or Technology Advancement Barriers and the Methodologies Used to Address Them:
Monitoring of chemical species in surrounding environments is crucial for the understanding of personal health and safety and is a key component in the ASSIST platform. Solid state based thin film sensors are favorable for real-time long-term environmental monitoring. Among various type of sensors, metal-oxide based thin film sensors are widely used but detection of gases rely on high temperatures (>300 °C) for sensitivity and selectivity to various gases. Existing sensors are typically using a substrate heating via metallic meanders to provide high temperatures at the cost of mW of power. Moreover, In order to improve sensitivity and the detection limit of the sensors, miniaturization (or reduction in size) is highly required. Therefore, development of nanoscale metal oxide gas sensors operated at room temperature or self-heating capability is a promising strategy that leads to improved performance and reduced power consumption in the µW range. Atomic Layer Deposition is the key technology for precise and uniform thickness control as well as for conformal coatings of high surface areas. Therefore, by combining high surface area structure with ALD metal oxide gas sensors, we can realize reliable and highly sensitive gas sensors having low power operation which leads to 100-1000 times reduction in device power. As an alternate approach, GaN based sensors are also evaluated. The main advantage of a GaN based sensor is the use of the 2 dimensional electron gas from the GaN/AlGaN interface enabling fast response to the surface change and hence increasing the sensitivity. Nanoscale GaN/AlGaN based...
sensors could reduce the sensor operating temperature (down to room temperature) and hence the total power consumption can be greatly reduced.

**Foreign Collaborations:** None to report

**Achievements in Year 3 and Previous Years:**

**NCSU Gas Sensor Testing Chamber Upgrade:** In year 2, we built a gas sensor testing system at NCSU capable of diluting gas sources from cylinders with zero grade air to generate concentrations of interest for sensor testing. This system had good capability for gases available in cylinders like CO and NO₂ but lacked the required functionality for ozone testing. This year, the NCSU testing system has been upgraded with a Teledyne T700U state of the art ozone generator and gas calibration mixer. This NIST certified unit, also used by the EPA in studies on the effects of ozone, is capable of producing ozone concentrations from 3 ppb to 1 ppm. We have verified the concentrations using electrochemical sensors from Alphasense similar to those we used to calibrate CO and NO₂ concentrations in years past.

![Figure 1](image.png)

Figure 1. (a) Grazing angle X-ray Diffraction results for ALD SnO₂. XRD results clearly show the crystalline nature of ALD SnO₂ thin film after 400 °C annealing. (b) ALD SnO₂ sensor transient response to 100 ppb ozone exposure. (c) Transient response of sensor with derivative (dR/dT).

**Metal oxide gas sensor:** In year 2, we experimented with ALD TiO₂ based thin film sensors and we found that ALD TiO₂ sensor required high temperature operation and base line drift was high. In Y3, we have explored SnO₂ as an alternative gas sensor for lower power operation. We have developed an ALD process for SnO₂ and have explored the material properties. Our results show that ALD SnO₂ thin film provides a good quality, poly crystalline, and stoichiometric oxide after
400C anneal as shown in Fig. 1 (a). We have fabricated ALD SnO$_2$ ultrathin film ($t_{\text{SnO}_2} = 6\text{nm}$) sensor and demonstrated sensor response to three consecutive 100 ppb ozone exposure (shown Fig. 1 (b) and (c)). It also found that ALD SnO$_2$ sensor has a higher conductivity resulting in a better signal to noise ratio and a film resistance that can be easily measured without applying heat to thermally generate carriers. Indeed we have observed room temperature response to low ppb levels of ozone using ultrathin ALD SnO$_2$ films. By applying an FFT filter to smooth the data and taking the derivative, we have demonstrated a correlation between ozone concentration and the maximum value of the derivative during the exposure. Figure 2 shows linear sensor response toward ozone down to 50 ppb at room temperature.

Finally, we have explored the specificity of our SnO$_2$ sensors. By operating at room temperature and limiting testing to concentrations found in the ambient, we have demonstrated that our SnO$_2$ sensors respond to ozone and selectively discriminate against CO and NO$_2$ as shown in Fig. 2 (b). Our SnO$_2$ sensors demonstrated no discernable response to 50 ppm CO and relative weak response to 100 ppb NO$_2$ when operated at room temperature. However, it is noted that the CO and NO$_2$ concentrations used in this study are pretty high that is not found in the ambient environment. However our demonstrated response to ozone concentrations does fall within environmental ranges indicating our sensor is a good candidate for ambient ozone sensing.

GaN/AlGaN semiconductor sensors: we have fabricated GaN/AlGaN semiconductor sensors with various active sensing areas. The device cross section and the microscopic images are shown in Figure 3 (a). The GaN surface was functionalized with 6nm of ALD SnO$_2$ to enhance the sensitivity. We have tested responses to three different environmental pollutants: CO (100ppm), NO$_2$ (100ppb), and O$_3$ (100ppb). The
devices are recovered after each test using UV LEDs to desorb the gasses from the active surface. The gas sequence was repeated for several temperatures from room temperature (RT) to 150°C. The response to the gas sequence at various temperatures is seen in Figure 3 (b). As substrate device operating temperature increases, the response to NO₂ and O₃ increases while CO does not demonstrate reducing response. Additionally, as the device is exposed to testing without reset, the magnitude of sensitivity decreases between each cycle and may be predicted by the slope shown in Figure 3 (c).

Summary of other relevant work being conducted within and outside of the ERC and how this project is different:
Metal oxide gas sensors have been actively and widely studied by numerous researchers. Within ASSIST center, Mayer’s group is developing nanowire metal oxide sensors by electrophoresis method, Oralkan’s group is examining resonant type gas sensors, and Muth’s group is fabricating
a tuning folk type sensor device. Our ALD based approaches can provide damage free and precisely controlled metal oxide films that are directly improving sensitivity and reduce the operation temperature of the sensors.

**Plans for the Next Year:**

*Metal oxide sensors:* suspended nanowire fabrication processes with structures defined through e-beam lithography and etching processes are being developed to create silicon nanowires coated with ALD metal oxides as well as pure metal oxide nanowires with thicknesses precisely controlled through ALD. Experimentation will determine ideal dimensions for the nanowires to optimize gas response and reduce power consumption.

*GaN/AlGaN sensors:* we will further increase the sensitivity of the device towards NO₂ by optimization of the SnO₂ thickness to ensure the response is a function of the 2DEG and reduce noise seen from the SnO₂ layer. Additionally, the device baseline resistance will be optimized by selective etching of the GaN cap/AlGaN layer and fabrication of three-terminal devices to provide 2DEG modulation

**Expected Milestones and Deliverables for the Project:**

The main deliverable for this project is to provide ultra-low power gas sensors for the ASSIST Gen 1 and 2 wearable platforms. The expected milestones for next year are following:

*Metal oxide sensors:*
- Demonstrate improved low power highly sensitive/selective metal oxide gas sensors
- Establish the gas sensing algorithms to enable to differentiate ozone concentration with the presence of other gases
- Develop composite metal oxide sensors and evaluate improvements in sensitivity and selectivity.

*GaN/AlGaN sensors:*
- Evaluate the effect of varying thicknesses of ALD SnO₂
- Develop low power GaN/AlGaN sensors with recessed structure
- Demonstrate GaN/AlGaN nanosensors

**Member Company Benefits:**

Member companies will benefit from the developed technologies because these enable low power operation, wearable form factor, and continuous monitoring of chemical species in surrounding environments.

If relevant, commercialization impacts or course implementation information: none yet