1. SEED GRANT OVERVIEW

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**Deployment of Soot-particulate Sensors in Flue-gas Stacks**

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<tr>
<th>Principal Investigator</th>
<th>Debbie G. Senesky, Ph.D.</th>
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<tr>
<td></td>
<td>Assistant Professor</td>
</tr>
<tr>
<td></td>
<td>Aeronautics and Astronautics Department</td>
</tr>
<tr>
<td></td>
<td>Stanford University</td>
</tr>
<tr>
<td></td>
<td>Email: <a href="mailto:dsenesky@stanford.edu">dsenesky@stanford.edu</a></td>
</tr>
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<tr>
<th>Co-Investigator</th>
<th>Stephen Luby, MD</th>
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<tr>
<td></td>
<td>Professor of Medicine</td>
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<tr>
<td></td>
<td>Infectious Diseases &amp; Geographic Medicine</td>
</tr>
<tr>
<td></td>
<td>Stanford University</td>
</tr>
<tr>
<td></td>
<td>Email: <a href="mailto:sluby@stanford.edu">sluby@stanford.edu</a></td>
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2. RESEARCH OBJECTIVE

Pollution from brick kilns in Bangladesh, especially particulate matter <2.5 µm causes thousands of premature deaths each year. The development of robust sensing technology can aid in real-time monitoring of flue and exhaust gases, which can help to improve combustion efficiency in kilns and guide regulatory efforts and enforcement. State-of-the-art sensors based on silicon technology are limited to temperatures below 200°C and are not suitable for monitoring flue exhaust conditions. As a result, new material platforms that utilize temperature-tolerant, ceramic semiconductor materials are proposed for flue emissions monitoring. Technology developed previously by the PI, has demonstrated the chemical and mechanical robustness of wide bandgap ceramic sensors at temperatures as high as 600°C and in dry steam. In addition, the polluting methods used in the manufacture of bricks in Bangladesh have been identified by the co-PI and there is a critical need to monitor and map these harmful flue gases for extended periods. In the proposed work, a micro-scale soot-particulate sensor that can withstand the harsh flue-stack environment will be developed to provide input data to long-term pollution data profiling, which do not yet exist for soot-particulate matter at a significant scale. The specific goals of the proposed research are to (1) design and fabricate a soot-particulate sensing system, (2) perform electrical characterization of the soot-particulate sensor operation using a soot particulate generator system (3) perform 100-hour durability tests of sensor components in an actual kiln and (4) lay the groundwork for deployment of the soot-particulate sensing system within brick kilns in Bangladesh for a proceeding 1-year pilot program. These tasks aid in the realization of advanced soot-particulate sensors for deployment within brick kilns as well as other large-scale soot-generating systems (e.g., industrial power plants, automotive exhausts). Ultimately, the sensor deployment technology developed in this interdisciplinary program can lead to a reduction in harmful emissions through data acquisition and analytics.

3. MOST SIGNIFICANT TECHNICAL ACHIEVEMENT(S)

- Designed and fabricated miniature soot sensor using metal-semiconductor interfaces and GaN-on-sapphire substrates.
- Generation of particulate matter 2.5 (PM$_{2.5}$) using a lab-scale miniaturized chimney. This system was used to characterize the sensor characteristic before deployment.
- Demonstrated recovery of operation of the micro-fabricated soot-particulate sensor after chemical regeneration at 550°C.
• Deployed sensors and sensor materials (GaN, SiC, Si and sapphire) in actual brick kilns located in Bangladesh to examine the material durability upon 100+ hours of exposure to different flue gas components.

4. ACTIVITIES AND ACCOMPLISHMENTS

Outcome #1, Design and Fabrication of a Soot-particulate Sensing System:

The designed soot-particulate sensor is composed of interdigitated (IDT) Pt electrodes on a GaN-on-sapphire (Al₂O₃) substrate to form a Schottky contact, as shown in Figure 1a. In this simple design, charged soot particles deposited on the sensor surface create electrical field effect on GaN surface and near the depletion region. Thus, particles deposited on lateral depletion region (uncovered by metal) and GaN surface affect the effective Schottky barrier height (SBH) and conduction band bending, respectively. This leads to a change in the current from the metal to the GaN substrate. Because the overall charge transport was limited by the Schottky contact, the current measurement was sensitive to change in SBH. Therefore, even a small number of soot particles can be detected by the direct deposition of soot particles near the lateral depletion region and on GaN surface, preventing the need for an initial accumulation of soot particles on the sensor surface to detect the change of resistance between electrodes by forming conductive pathways in conventional devices. To estimate the depletion width and the change of SBH in an ideal Schottky diode, the equilibrium energy band diagram, as shown in Figure 1b, can be utilized.

![Figure 1: (a) Schematic of the Pt-GaN soot-particulate sensor and cross-sectional view of the device. (b) Energy band diagram change with respect to the positively charged soot particles on the (i) lateral depletion region and (ii) GaN surface.](image)

To microfabricate the soot-particulate sensor, a GaN-on-sapphire substrate was spin-coated with a 1 µm–thick positive photoresist at 5500 rpm for 30 s, and the sample was prebaked at 90°C for 1 min. The pattern of IDT electrodes was then exposed to UV light via a standard soft-contact photolithography aligner. Developer was used to remove the exposed IDT electrodes pattern. After rinsing the sample in deionized water, a 40 nm–thick Pt metal film was deposited on the patterned sample via the electron beam metal evaporation, and a lift-off process in acetone with sonication was performed to remove unwanted metal on the photoresist. The sample was finally annealed (preconditioned) at 500°C for 3 h before testing.

To deposit soot-particulate matter on the fabricated sensor, a laboratory-scale miniaturized chimney was installed using a beaker, funnel, and compressed-air tank, as shown in Figure 2a. Commercially available paraffin candles were used to generate soot-particulate matter. The fabricated sensor was placed at the end
of the funnel outlet to protect the sensor from the high temperature of the candle flame (typically near 1400°C), which may induce device failure by thermal shock, degradation, or oxidation of the Pt metal. Figure 2b shows the soot-particulate sensor fabricated on 1×1 cm² GaN-on-sapphire substrate before and after 100 µg soot accumulation.

Figure 2: (a) Image of the miniaturized chimney to deposit soot particles on the sensor. (b) Image of the fabricated sensor on GaN-on-Sapphire before and after soot accumulation.

Outcome #2, Electrical Characterization of Soot-particulate Sensor:
Figures 3 shows the scanning electron microscope (SEM) images of the Pt IDT electrodes on the GaN layer after the deposition of 50 µg of soot particles using the miniaturized chimney system. The SEM image shows uniform and conformal accumulation of fine soot particles with diameters ranging from 30 to 50 nm was achieved along the electrodes, as shown in Figures 3b and 3c. This confirms that the size of the particles generated is within the PM₂.₅ particulate class, which is a main target for many soot particulate sensing applications. Individual particles were aggregated side by side, forming a chain-shaped cluster, because soot particles have both positively and negatively charged particles, which can induce aggregation of particles due to Coulomb interactions.

Figure 3: (a) SEM image of the interdigitated electrodes on GaN layer after soot accumulation. (b) and (c) SEM image of soot-particulate matter deposited on the sensor.

To characterize the fabricated soot-particulate sensor based on a Pt-GaN Schottky interface, the current-voltage response was measured using a high-temperature probe station and semiconductor device analyzer. Figure 4 shows the change of current through the GaN layer between IDT electrodes before and after 10 µg of soot accumulation. As a result, the current of 816.2 µA at 3 V was increased to 1172 µA (i.e., ~43.6% increase) after soot accumulation, because positively charged soot particles induced conduction band bending and the SBH change at the interface of the Pt-GaN layer. Based on the
relationship in thermionic-emission theory and experimental data, it was found that the SBH was reduced by approximately 1.1 meV upon exposure to soot-particulate matter. The change is relatively small compared to those of gas sensors (order of ~10 meV).

To demonstrate the ability of regeneration, the chuck in the probe station was heated to 550°C and held for 10 minutes to oxidize soot particles and any other contaminants on the sensor, and the sensor was then cooled down to the ambient temperature. After taking SEM images of the regenerated sensor, no soot particle was detected on the sensors, they were clear as initial. The sensing signal was measured again before and after soot accumulation. The results in Figure 4 show that the overall value of the reference current for all voltage ranges was lower than the reference current before regeneration (square-solid line), which might be caused by increased contact resistance due to high temperatures (e.g., oxidation of Pt/GaN interfaces) and tend to saturate near 550 µA at 3 V after several regeneration processes. After the second soot accumulation on the sensor, the sensing current was increased from 582.3 µA at 3 V to 892.8 µA again, showing the recovery of sensitivity, and, therefore, demonstrating the stable operation of the sensor in harsh, particulate-rich environments.

Figure 4: Measured current-voltage response of soot sensor based on Pt-GaN Schottky contact before and after regeneration at 550°C under forward bias.

Outcome #3, Deployment of Soot-particulate Sensor Materials within Brick Kilns in Bangladesh:

Around 92% of the kilns for manufacturing bricks in Bangladesh are of the severely polluting, energy intensive Fixed Chimney Kiln (FCK) type (Fig. 5a). The other types such as Zigzag Kiln, Hybrid Hoffmann Kiln (HHK), Vertical Shaft Brick Kiln (VSBK) are less polluting but capital intensive, hence only comprise the remaining 8%. For this study, we deployed our sensor materials in an FCK (Figs. 5b and c) located in the Savar district, Dhaka city, Bangladesh, owned by Mr. Asadur Rahman, Vice President, Bangladesh Brick Manufacturing Owners Association (BBMOA).

For effective sensing, the micro-fabricated soot sensor needs to be placed in close proximity to the flue gas vent chimneys, while keeping a safe distance to limit temperatures below 550°C and ensure safe operation of the device. Besides particulate matter (PM2.5), the flue gases from brick kilns also contain other harmful gases (SO2, NOx) due to burning of impure coal in a combustive environment. Hence it is crucial to study the sensor material stability to these emissions. We chose five samples for each test device: (i) Si, (ii) SiC, (iii) Sapphire, (iv) GaN-on-sapphire, (v) Pt/GaN-on-sapphire (soot sensor). They are housed in a brass holder machined at the Stanford Machine Shop (Fig. 5d). Three such test devices were prepared and deployed at three different locations on the chimney between August 24-25, 2015.
The first device was placed at the chimney base (Figs. 5e and 5f), where the flue gases from different combustion chambers join to enter the chimney. The second and third devices were placed at heights of about 17 feet and 27 feet from the chimney base, through narrow openings made into the chimney wall which is about 20-25 inches thick. Iron rods were used to mount the test devices and provide support during operation of the kiln. Post installation, the kiln was fired on November 13, 2015, and the devices were then removed on November 21, 2015 after 8 days (192 hours) of continuous exposure to high temperatures, soot, and flue gases, as shown in Figs. 5(g-i). The exposed samples are being shipped to Stanford, where they will be further analyzed using chemical, surface, and electrical analysis to characterize material degradation and sensing response. With this knowledge, the next generation of soot sensors can be developed for enhanced robustness and stability.

Figure 5: (a) Schematic of a fixed chimney kiln (FCK) showing the different combustion chambers and the flue gas flow into the chimney and exit to atmosphere. [GreenTech report, 2013] (b) Image of the FCK in Savar area used for this study, showing bamboo scaffolding used to climb the chimney for deployment. (c) Close-up image of personnel deploying a device at a height of 27 ft from the base. (d) Picture of the sensor test device prepared at Stanford. (e) Picture of personnel installing a device at the
chimney base. (f) Picture of device at the chimney base, facing the direction of flue gases. (g-i) Pictures of device after 8 days of exposure to high temperature, soot, and flue gases.

5. FUTURE WORK/OUTLOOK FOR SOOT PARTICULATE SENSOR RESEARCH

Through this seed program, we experimentally examined the electrical characteristics of soot-particle sensors in experimental environments. In addition, we deployed actual sensors and sensor materials for feasibility/reliability tests in kilns located in Bangladesh. Upon further examination of the materials the appropriate sensor packaging and interface electronics will be determined. A future strategy for soot-particle sensor deployment is outlined below.

- Perform further sensor characterization to create detailed maps of soot-particle concentration and I-V characteristics at various temperatures.
- Explore the use of 3D sensor architectures to increase sensor surface area and improve sensor sensitivity.
- Package sensors (soot-particle and temperature) with power management and interface electronics for periodic, wireless communication of sensor data.
- Develop improved deployment strategies to enable sensor insertion at the top of the brick kiln and within multiple brick kilns. For example, leverage Unmanned Ariel Vehicles (UAVs) or “Wonder Climbers” (tree climbing robots) that can readily access the brick kilns to deploy sensors and periodically collect sensor data. It should be noted that UAVs/drones are not currently permitted in Bangladesh and permission is required.
- Larger deployment effort (across South Asia) including power plants and propulsion systems (automotive and aircraft exhaust) to capture big data on the soot-particle emissions.

Ultimately, the work spawned from this program will enable scientists to better measure emissions that have a substantial effect on the environment and health and use this information to guide approaches to reduce these impacts.

6. CONFERENCES


7. PUBLICATIONS


8. NEW TECHNOLOGY, REPORTABLE ITEMS, INVENTIONS, AND PATENTS

9. POSTDOCTORAL RESEARCHER(S) / STUDENT(S)

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<th>Assistance Type</th>
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<tr>
<td>Postdoctoral</td>
<td>1</td>
<td>Dr. Hongyun So (Stanford Team), Development of soot sensor element</td>
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<tr>
<td>Graduate</td>
<td>1</td>
<td>Mr. Sambhav Jain (Stanford Team), Test planning and deployment of sensor materials in Bangladesh</td>
</tr>
<tr>
<td>Research Investigator</td>
<td>1</td>
<td>Mr. Debashish Biswas (Dhaka Team), Deployment of sensor materials in Bangladesh</td>
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