Wireless 3D Nanorod Composite Arrays based High Temperature Surface-Acoustic-Wave Sensors for Selective Gas Detection through Machine Learning Algorithms

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Presentation Outlines

- Project Description and Objectives
- Background and Project Update
- Preparing Project for Next Steps
- Conclusions and Acknowledgement

Project Description and Objectives

- **Objectives of Project**

To develop a new class of wireless 3D nanorod composite arrays based high temperature surface-acoustic-wave (SAW) gas sensors for selective and reliable detection through machine learning algorithms

- **Our Strategies**

1. High-temperature stable passive wireless SAW sensor arrays
2. High-temperature stable perovskite coated three-dimensional (3D) metal oxide nanorod composites
3. Machine learning algorithms

Project Description and Objectives

- **Strategic alignment of project to Fossil Energy objectives (Sensors and Controls)**

1. The proposed high temperature sensing platform specifically provide a novel, feasible, and functional device well-suited for the development of in-situ and real-time high temperature gas sensing.
2. If successful, this approach could become a new standard for high temperature environmental sensing and the sensor signals can provide useful information for combustion control.
3. The realization of this new class of nanorod composite array based high temperature gas sensors could provide an easy platform for directly adapting to wireless communication for remote monitoring of sensing signals, thus could bring a potential leap in various combustion monitoring and control devices development.
4. With the successful demonstration of the wireless 3D nanorod composite SAW sensor array and the development of advanced machine learning algorithm, the proposed sensing platform could realize in-situ and real-time monitoring and control of complex combustion environments.

Background and Project Update

Environment & Energy Concerns

- Better control of **combustion**
- Reduction of **emissions** (CO, NO_x, SO_x, HCs) ➡ less environmental problems
- Improvement of **energy efficiency** ➡ more energy savings

❖ **Contribution from HTGS and Controls**

Value Derived for an Existing Coal Fired Power Plant

FUEL COSTS
$39 Million/Year ➡

➡ **Gaseous Emissions**

➡ **POWER**
3,285,000,000 kw-hr/yr
@75% Capacity Factor

➡ **Solid Wastes**

Total Fuel + O&M Budget $45 Million - Avg. 500 MW Unit (Analysis for 2000)

➢ **1% improvement in EFFICIENCY**

- $390,000 savings in fuel per year **600**
- $4.1 million for entire installed fossil capacity

➢ **1% REDUCTION in greenhouse gases and solid wastes**

DOE prediction:

Energy savings per year

0.25 quadrillion BTU

- 11 million tons of coal
- 250 billion cubic feet of natural gas
- 43 million barrels of crude oil

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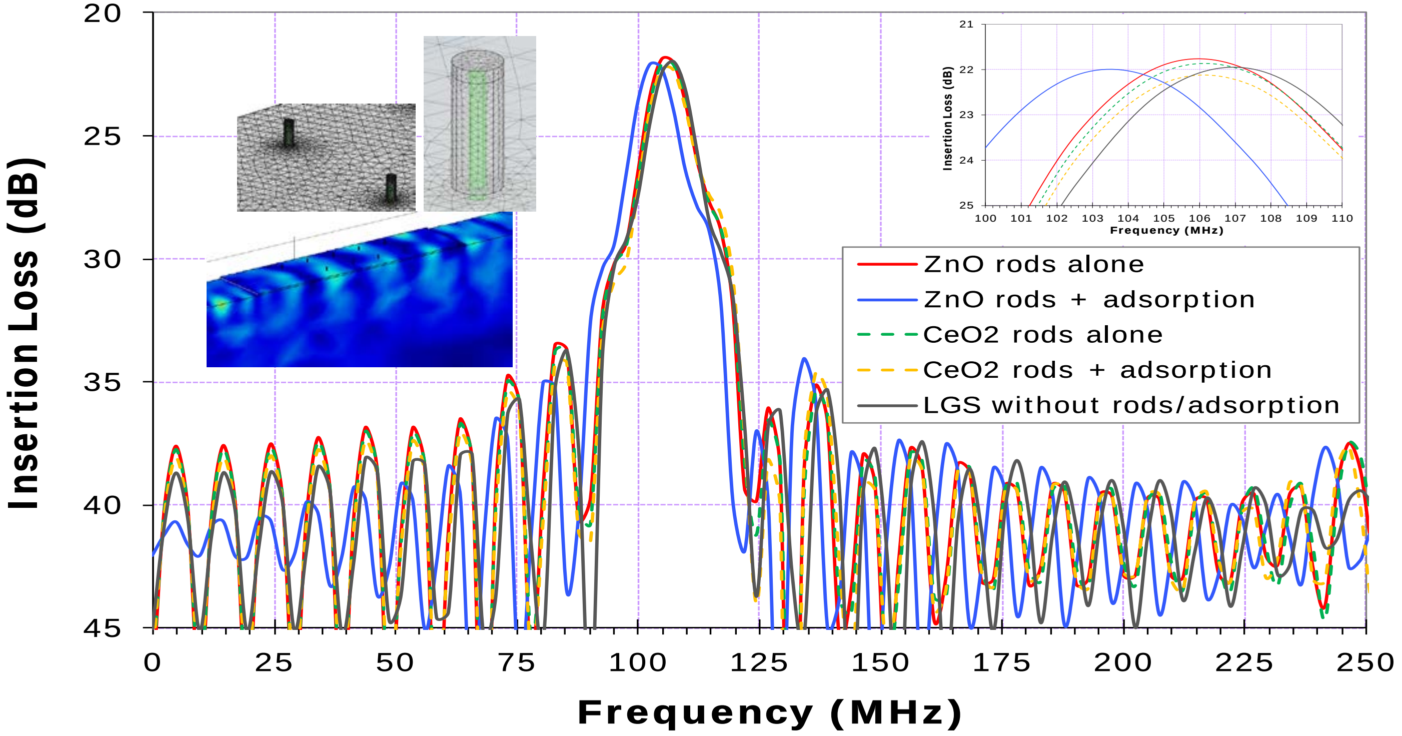
Why surface-acoustic-wave (SAW) gas sensor?

- SAW sensor has been explored in high temperature gas detection because SAW devices are sensitive for discriminating any surface perturbation (chemically or physically) such as molecule adsorption and conductivity changes produced by chemisorption.
- SAW devices are also inexpensive in large scale fabrication. In recent years, a range of high-temperature stable piezoelectric materials have been developed including langasite (LGS), gallium phosphate (GaPO4), and aluminum nitride (AlN).
- Among all these materials, LGS has been intensively investigated for high temperature SAW-based temperature sensor because it does not undergo a phase transition up to its meting temperature at 1470 °C and the LGS-based SAW device has been operated at 800 °C for more than 5.5 months, showing very good stability.

Background and Project Update

Why surface-acoustic-wave (SAW) gas sensor? (Cont'd)



Simulated insertion loss vs. frequency spectra obtained for a LGS SAW sensor enhanced with ZnO or CeO_2 nanorods. Left inset shows the SAW traveling near the active surface and close views of nanorods. Right inset shows the peak region of the spectra.

Background and Project Update

Why hydrothermal method to prepare 3D metal oxide nanomaterials?

- Vapor-phase-transport method and sol-gel method have been developed to synthesize 3D metal oxide nanostructures, their application to large scale production of 3D arrays are greatly limited due to the low reproducibility, high-cost, and/or complicated procedures.
- Hydrothermal method has emerged lately as an alternative for large-scale, cost-effective and reproducible production of 3D nanostructures.
- Many 3D metal oxide nanorods have been synthesized using hydrothermal method by our group and other groups, such as CeO_2, ZnO, SnO_2, TiO_2, etc.
- Our team has demonstrated that the 3D metal oxide nanorods can serve as scaffolds for subsequent highly stable perovskite nanoshell coating, thus generating 3D nanocomposites with super high-temperature stability and/or gas selectivity.

Background and Project Update

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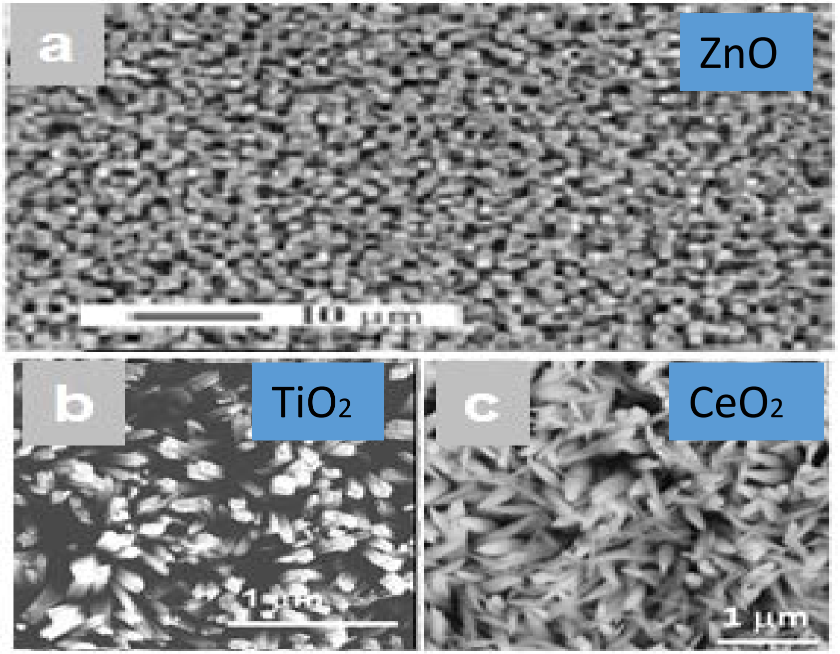
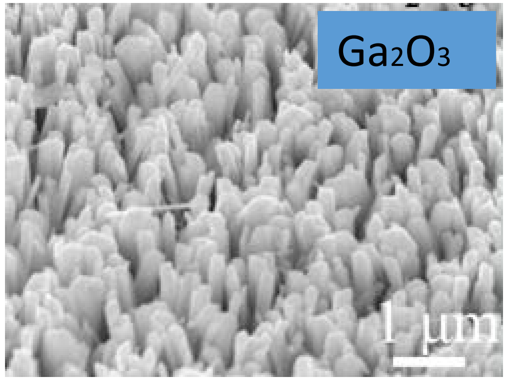
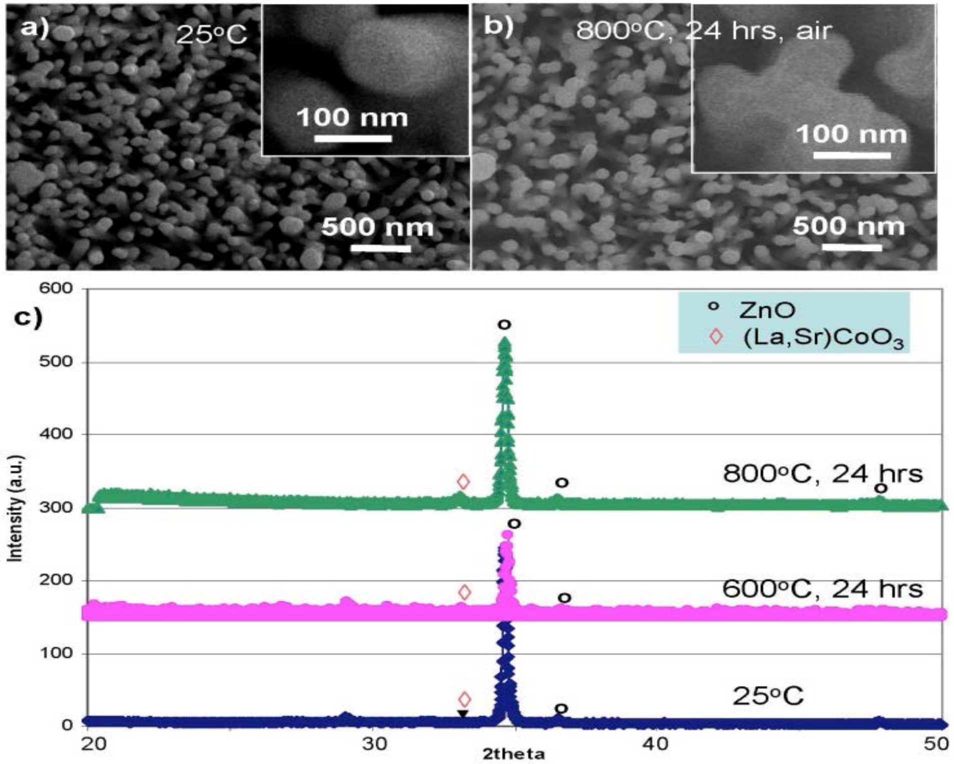
Why hydrothermal method to prepare 3D metal oxide nanorod arrays? (Cont'd)





Why hydrothermal method to prepare 3D metal oxide nanorod arrays, followed by perovskite coating?



a) and b) are respectively a typical SEM image of ZnO/LSCO heterostructured nanorods before and after 24-hour 800 °C thermal aging experiment. c) is a set of comparative XRD spectra scanned for the ZnO/LSCO heterostructured nanorod arrays after 24 hours' thermal aging at temperatures up to 800 °C.

Background and Project Update

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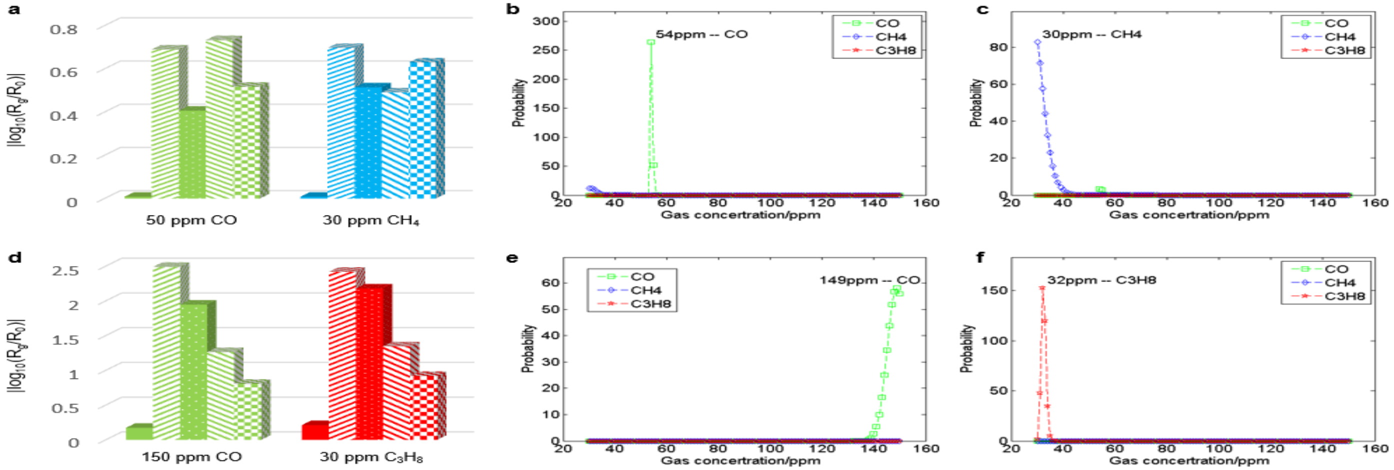
Why machine learning algorithms for improved identification of target species and concentration?

- A sensor array could provide a specific and unique response patterns (fingerprints) for different individual chemical species or mixtures of species.
- With subsequent data analysis, the gas sensor array could be used to qualitatively identify gas species using pattern recognition approaches and quantitatively determine gas composition based on learning and regression methods.
- We can think of a learner as an entity that tries to guess a concept or function. Let this function be f(x1, x2, …, xn) where x1, x2, …, xn are the underlying variables. A learner is supplied with examples. An example is nothing but a specific assignment of values to the variables and the corresponding value of the function.
- After having seen a sufficient number of examples, the learner comes up with an estimate of the function. In general the estimate may not be the same as f but possibly a close approximation to f.

Background and Project Update

Why machine learning algorithms for improved identification of target species and concentration?



A case study using a simple algorithm: The comparison of sensor array response input of a) 50 ppm CO and 30 ppm CH_4, d) 150 ppm CO and 30 ppm C_3H_8. The output of gas identification program for b) 50 ppm CO, c) 30 ppm CH_4, e) 150 ppm CO and f) 30 ppm C_3H_8, respectively.

Gas concentration predicted by gas identification program

Gas Type	CO				CH_4				C_3H_8			
Real Conc./ppm	50	80	100	150	30	50	80	100	30	50	80	100
Predicted Conc./ppm	54	72	104	149	30	51	77	101	32	45	81	100

Our Proposed Main Activities

1. High-temperature stable passive wireless SAW sensor arrays
2. High-temperature stable perovskite coated three-dimensional (3D) metal oxide nanorod composites
3. Machine learning algorithms

Background and Project Update

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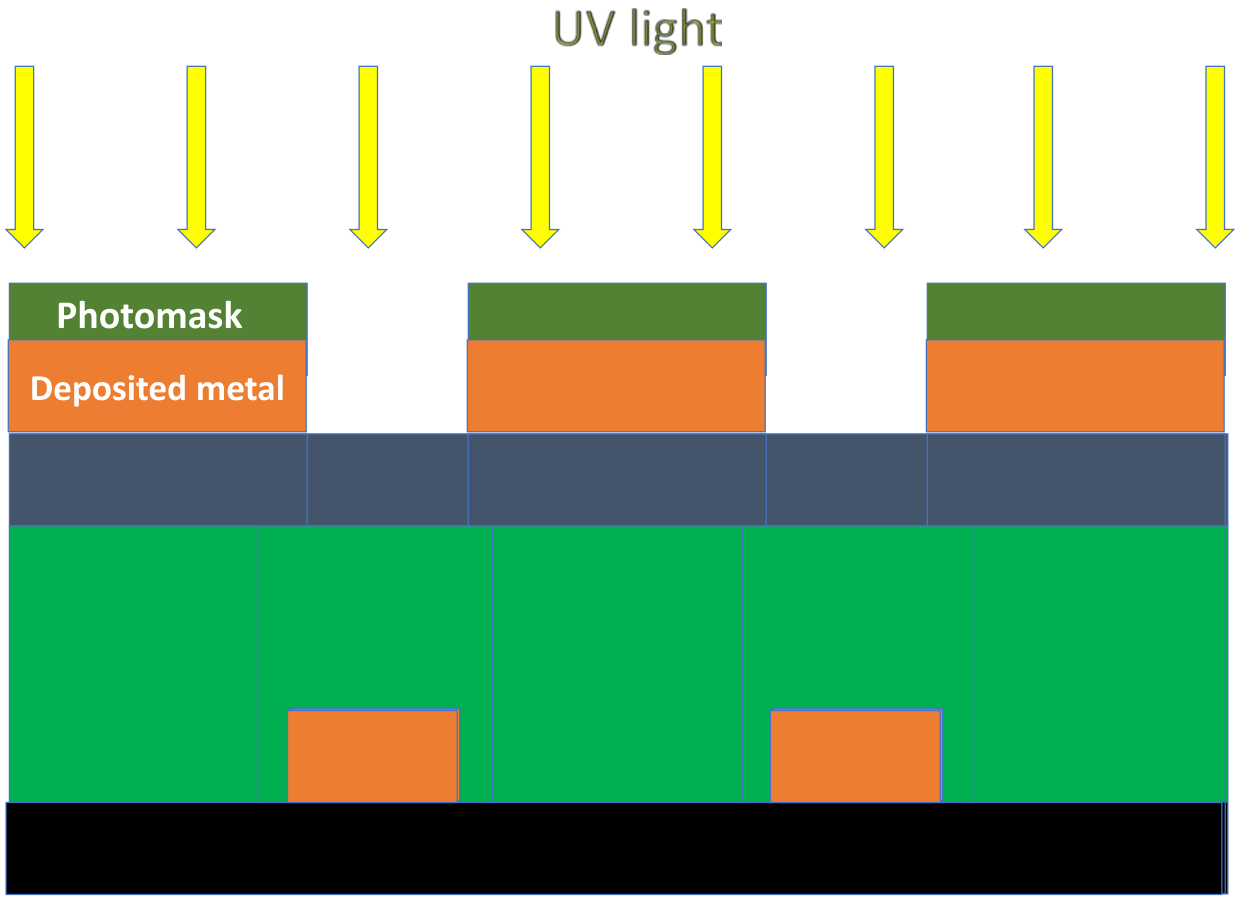
1. Design, fabrication, and characterization of a passive wireless SAW arrays on LGS substrate

- The bilayer stack including LOR resist beneath Shipley S1805 photoresist for metal lift-off processing
- Compared to using Shipley photoresist alone, LOR (Lift-Off Resist) creates a sufficient gap between the metal areas to ensure a good lift-off → The metal on the surface of the wafer must not connect the metal on the top of the resist

**** Minimum feature size: 2 µm***

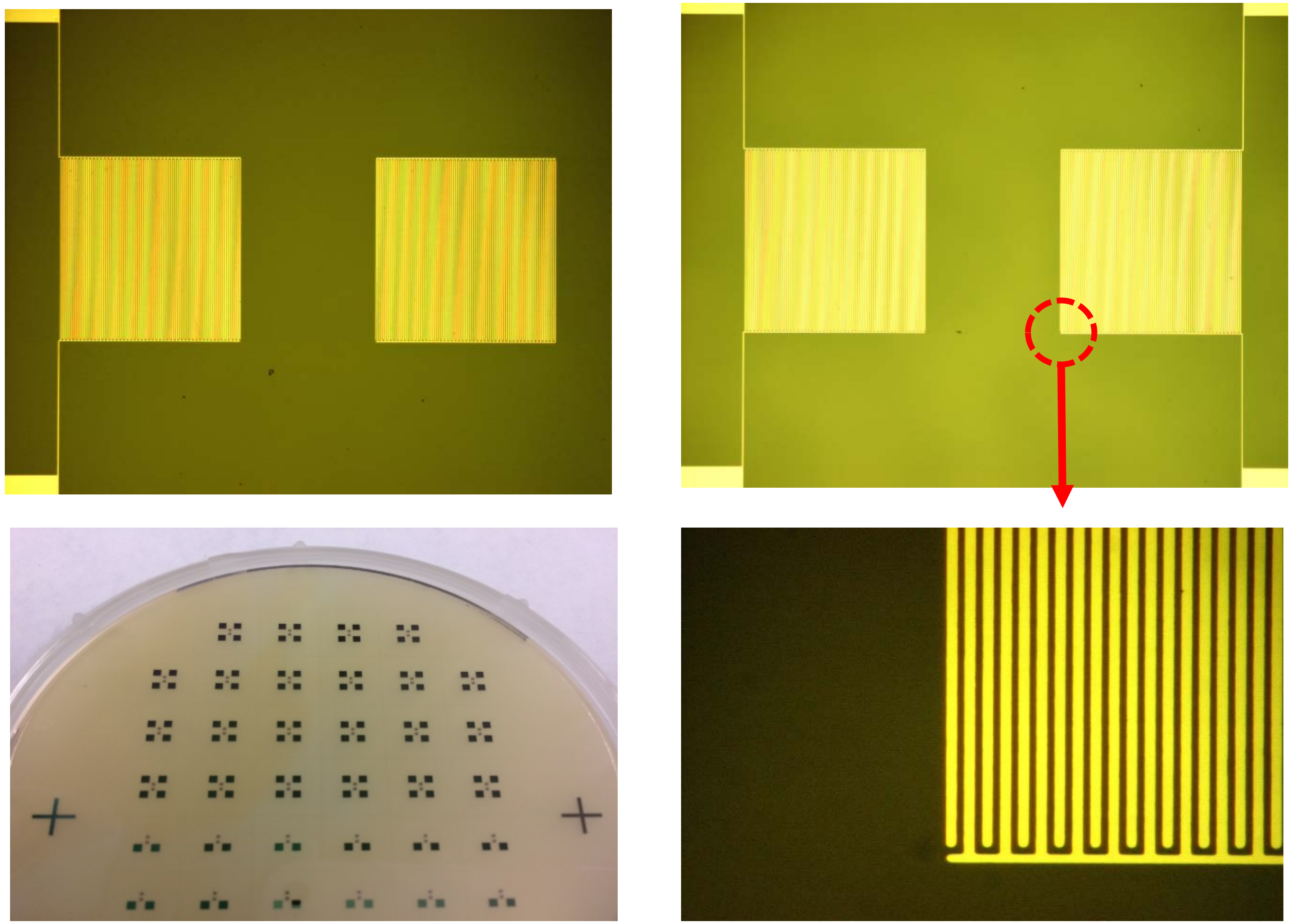


The general lift-off process (positive)

Background and Project Update

NATIONAL ENERGY TECHNOLOGY LABORATORY

1. Design, fabrication, and characterization of a passive wireless SAW arrays on LGS substrate



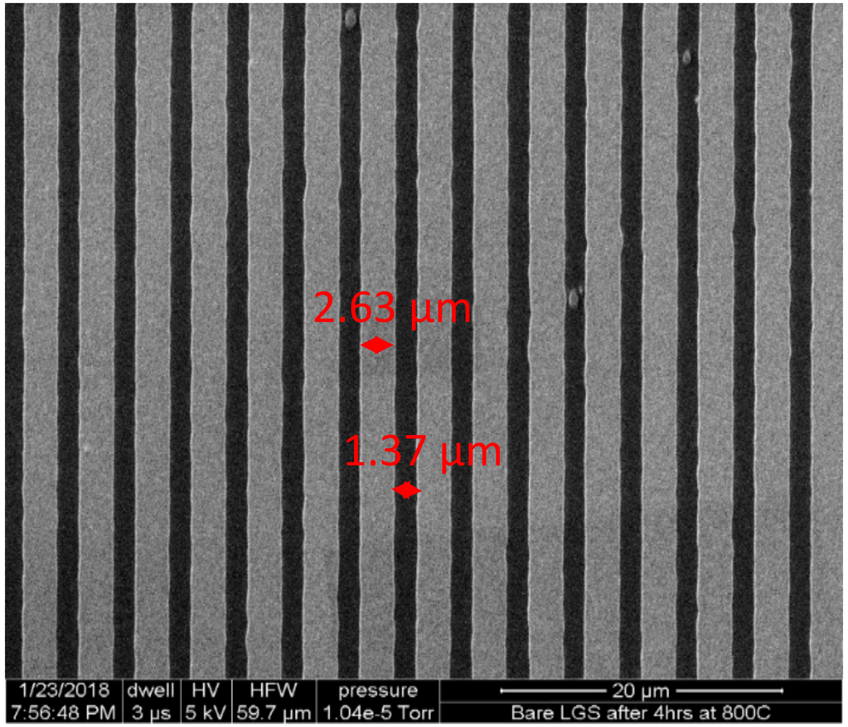
- SAW circuits with designed feature size of 2 μm were fabricated on LGS wafer.

Background and Project Update

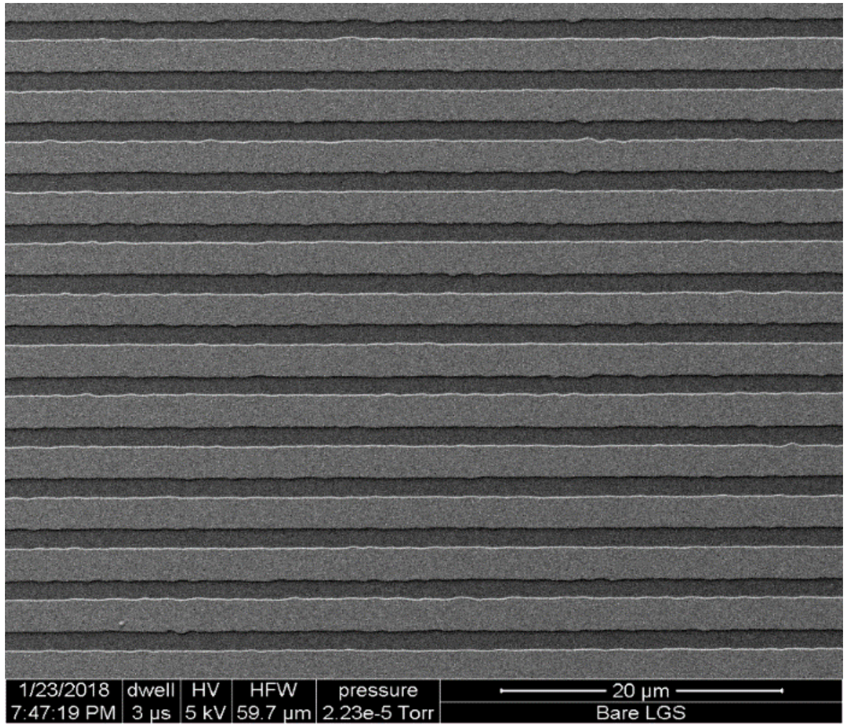
NATIONAL ENERGY TECHNOLOGY LABORATORY

1. Design, fabrication, and characterization of a passive wireless SAW arrays on LGS substrate

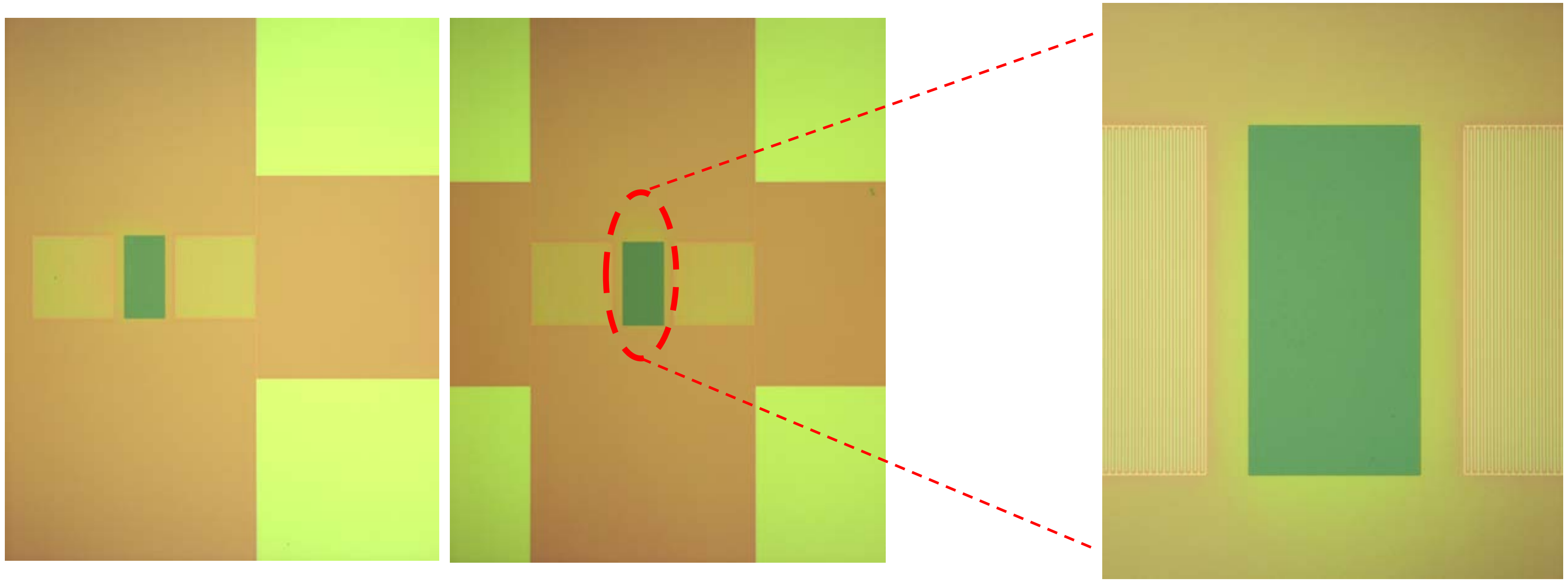
Before thermal treatment



After thermal treatment (4 hrs at 800 °C under air atmosphere)



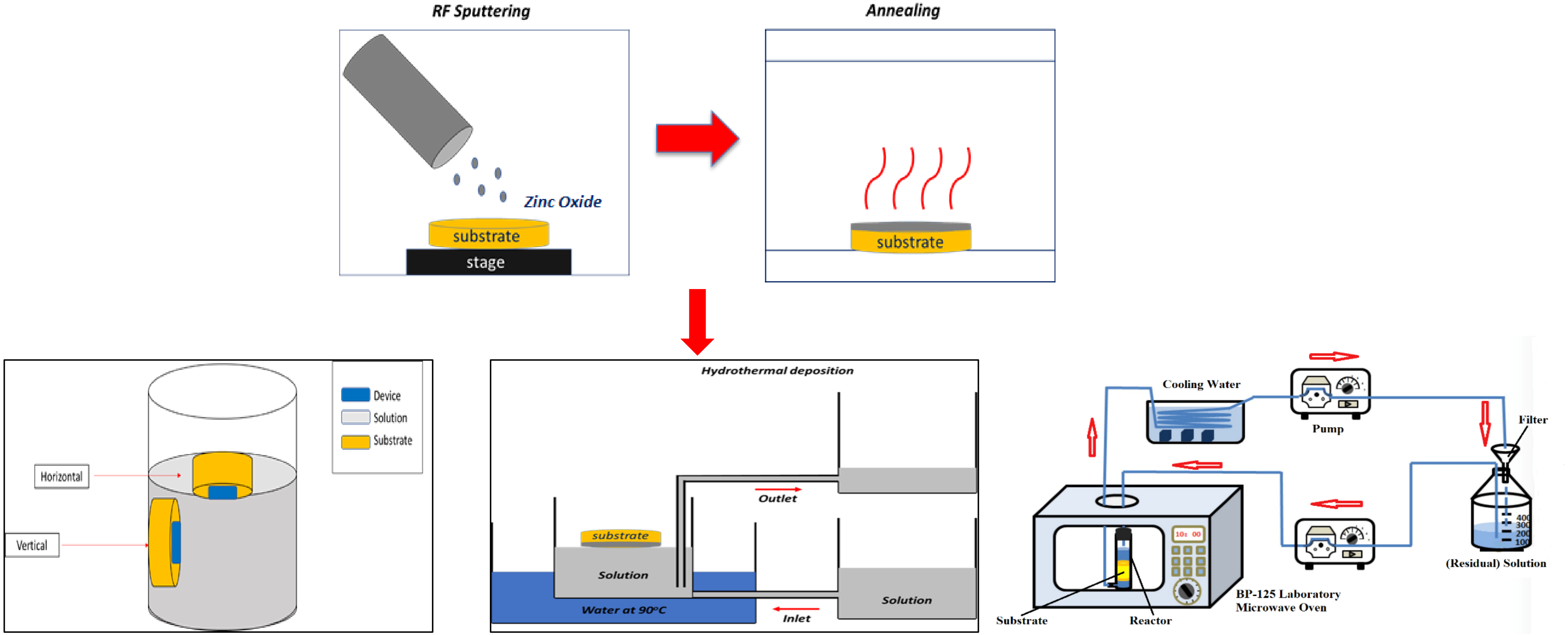
1. Design, fabrication, and characterization of a passive wireless SAW arrays on LGS substrate



Deposit the 2nd photoresist layer using maskless alinger to only expose the sensing area to the environment for selective growth of 3D nanowires.

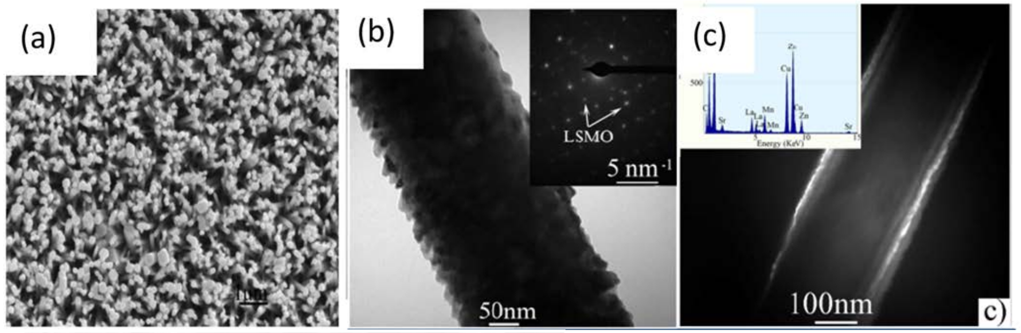
Background and Project Update

2. *In-situ hydrothermal growth of 3D metal oxide nanorods on the active sensing area of SAW sensors followed by perovskite nanosheath coating*

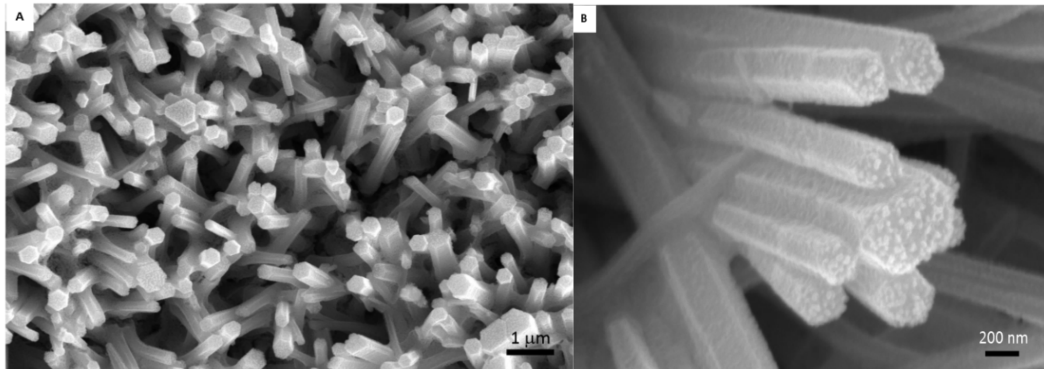


Background and Project Update

2. In-situ hydrothermal growth of 3D metal oxide nanorods on the active sensing area of SAW sensors followed by perovskite nanosheath coating (cont'd)



LSMO on ZnO nanorods

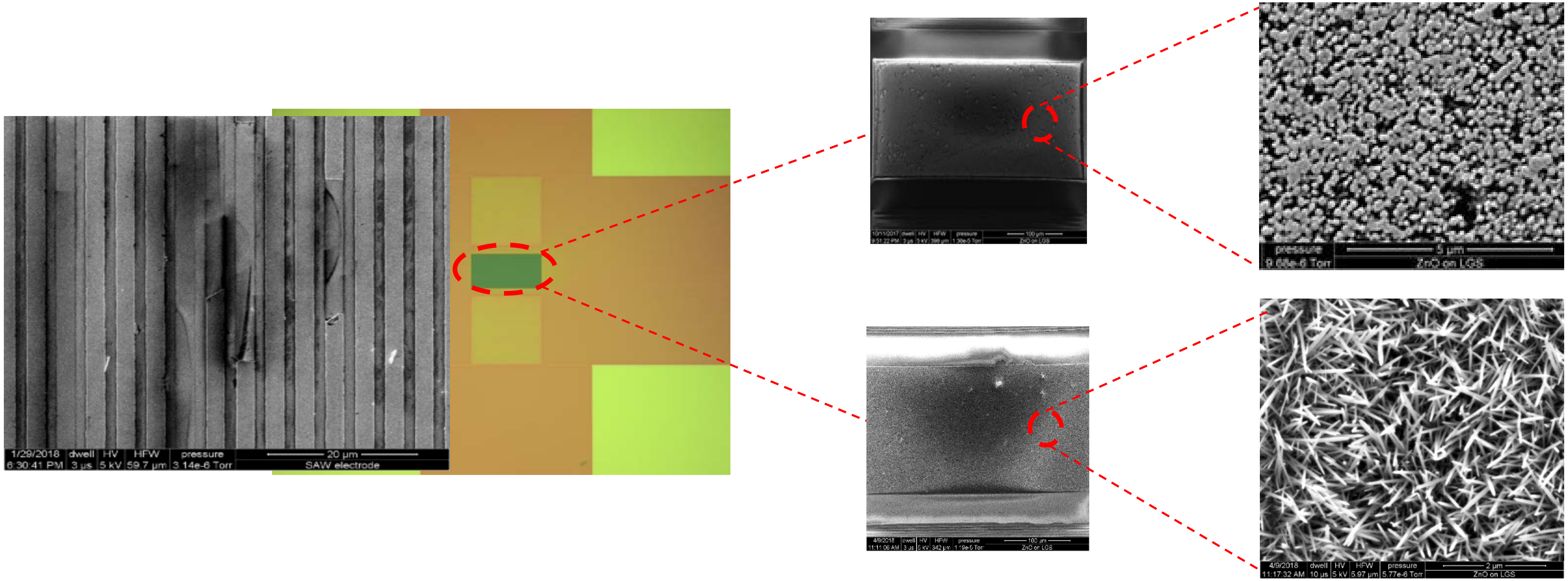


LSCO on ZnO nanorods

Thermally stable perovskite could help stabilize metal oxide nanorods such as ZnO, allow them to work at higher temperature than them alone.

Background and Project Update

2. In-situ hydrothermal growth of 3D metal oxide nanorods on the active sensing area of SAW sensors followed by perovskite nanosheath coating (cont'd)

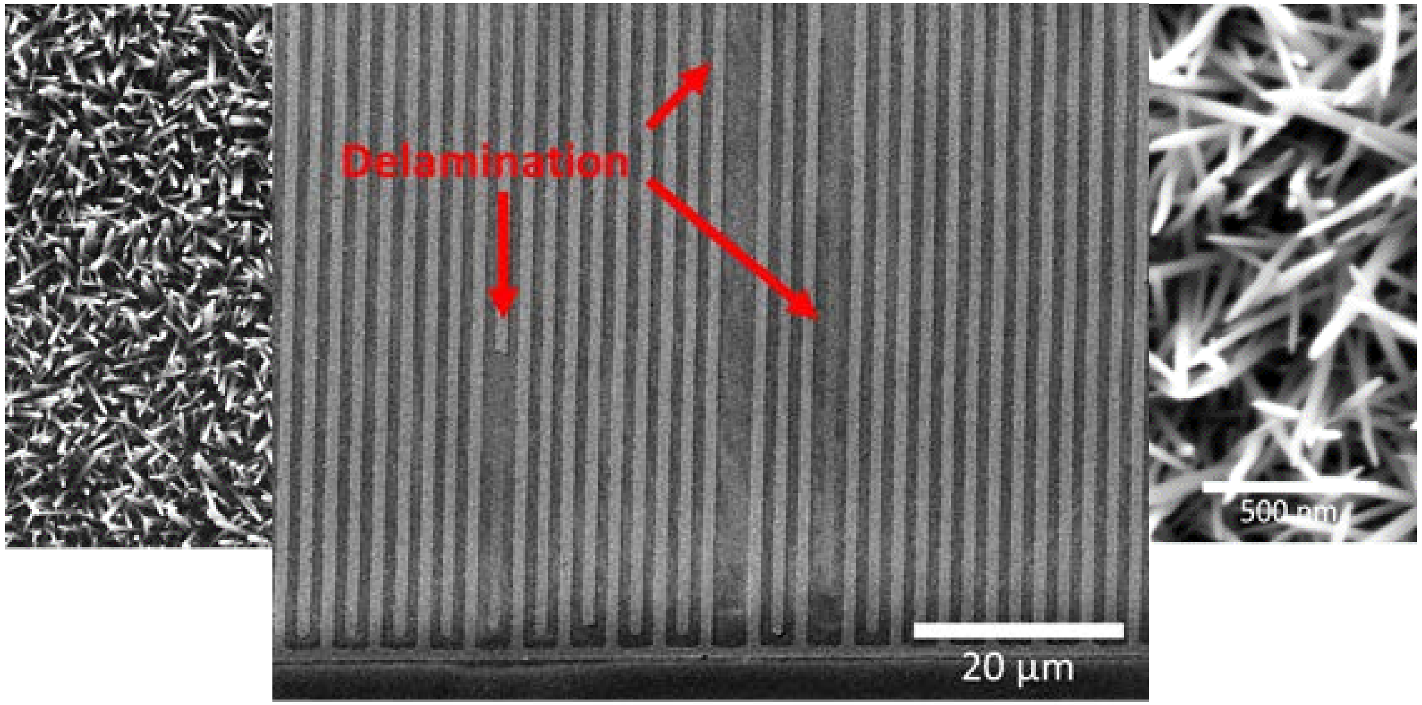


Selective growth of metal oxides on the sensing area

Background and Project Update

2. In-situ hydrothermal growth of 3D metal oxide nanorods on the active sensing area of SAW sensors followed by perovskite nanosheath coating (cont'd)

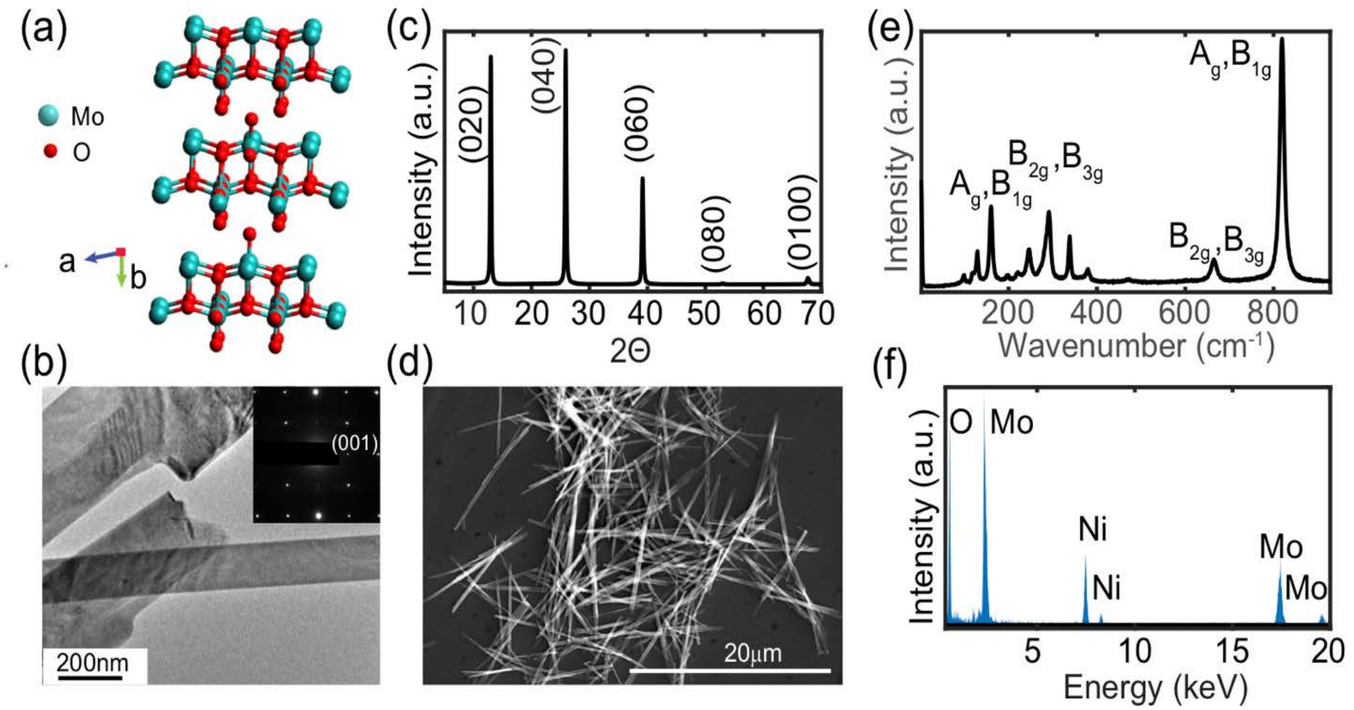
1.5 μm (vs. 0.5 μm in previous study)

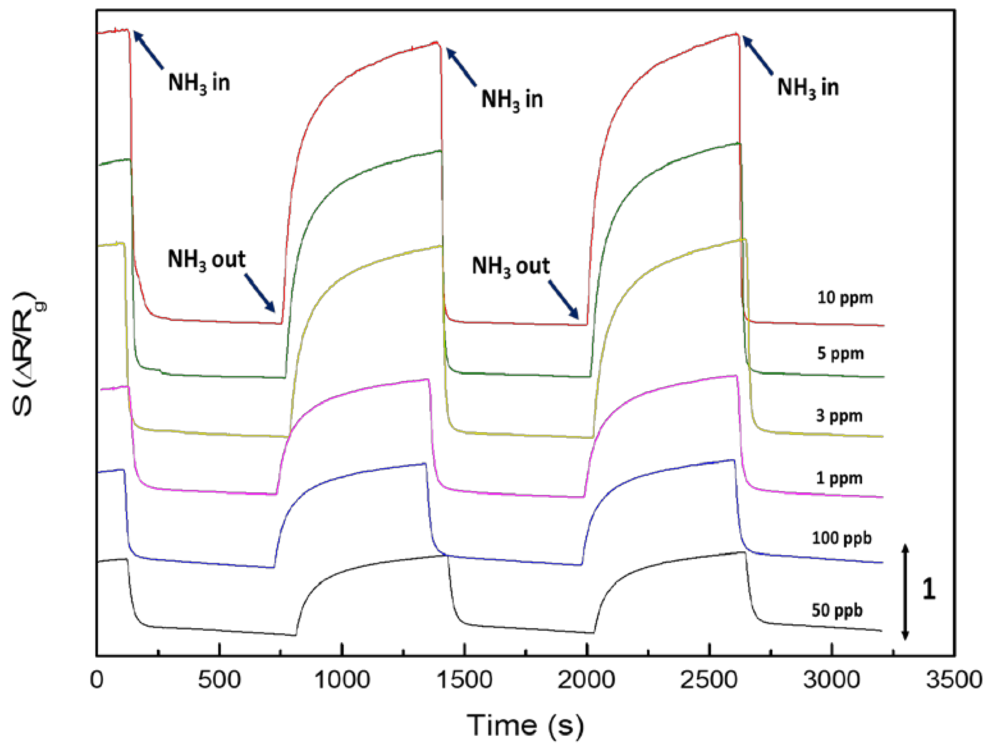


Background and Project Update

3. Drop-casting method used for selective deposition of metal oxides on the sensing area

NH3-selective MoO3 nanoribbons



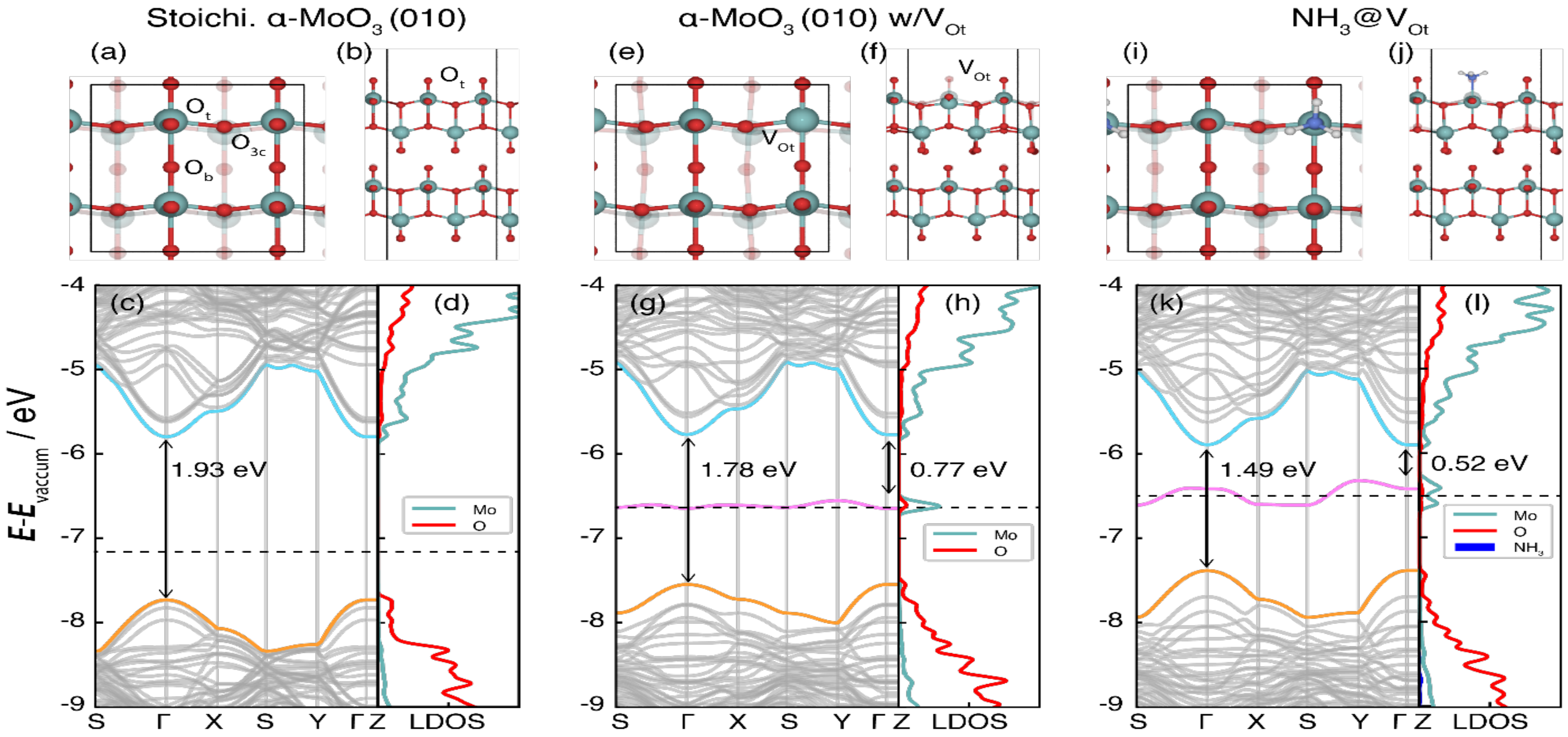


Kwak, et al. ACS Appl. Mater. Inter. 2019.

Background and Project Update

3. Drop-casting method used for selective deposition of metal oxides on the sensing area

NH3-selective MoO3 nanoribbons

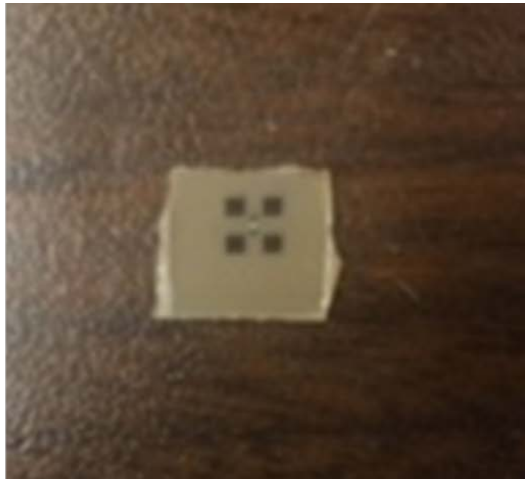


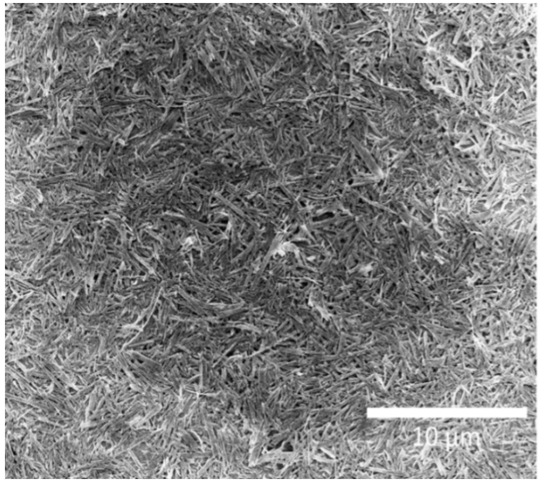
Density functional theory (DFT) simulations with Hubbard U and Van der Walls correction were employed to understand the adsorption of gas molecules on the α-MoO_3 (010) surface and the corresponding alternations in electronic structures.

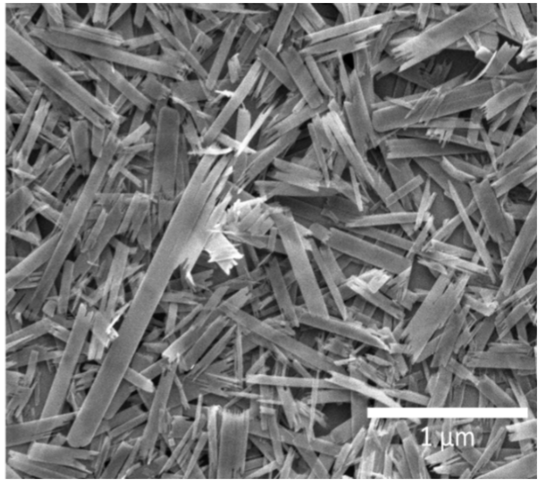
Kwak, et al. ACS Appl. Mater. Inter. 2019.

Background and Project Update

3. Drop-casting method used for selective deposition of metal oxides on the sensing area

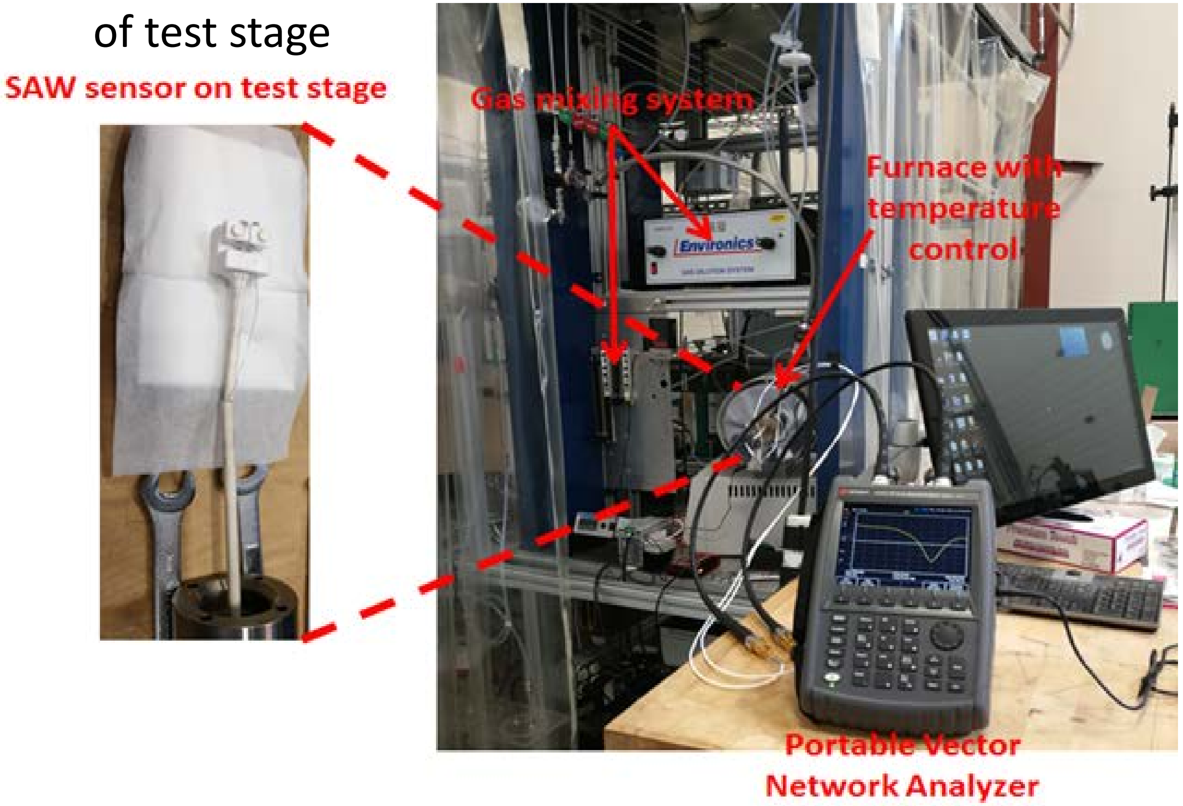


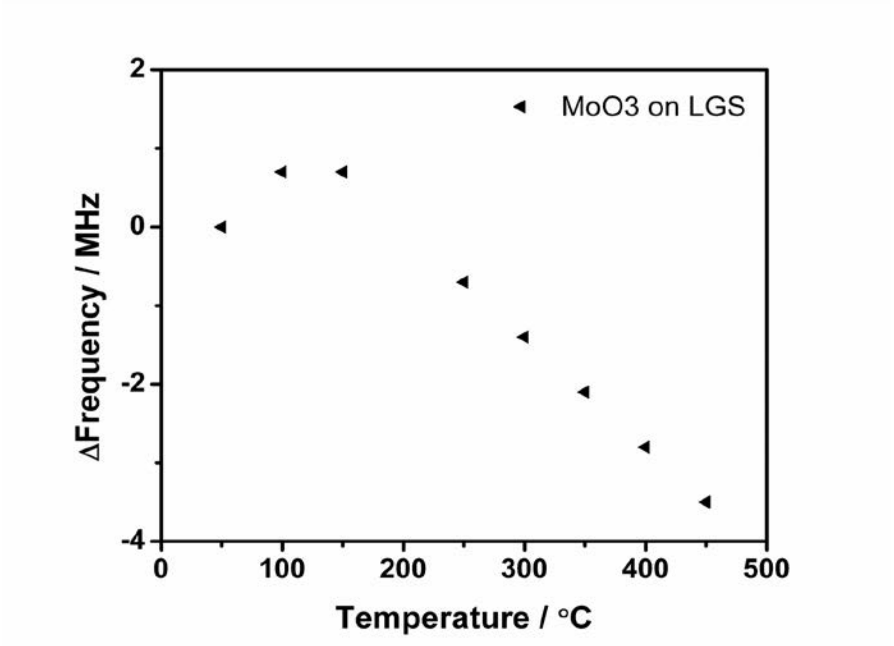




4. SAW sensor experiment setup

1st generation
of test stage





Resonant frequency change of the drop-cast MoO_3 based LGS SAW sensor as a function of temperature

Background and Project Update

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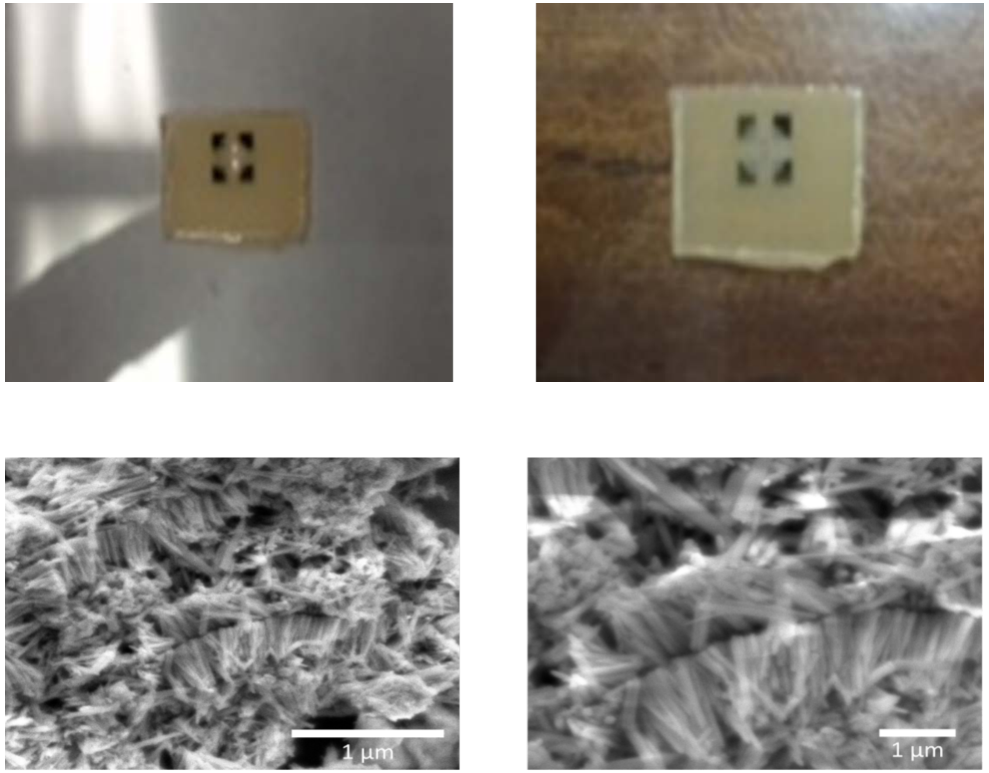
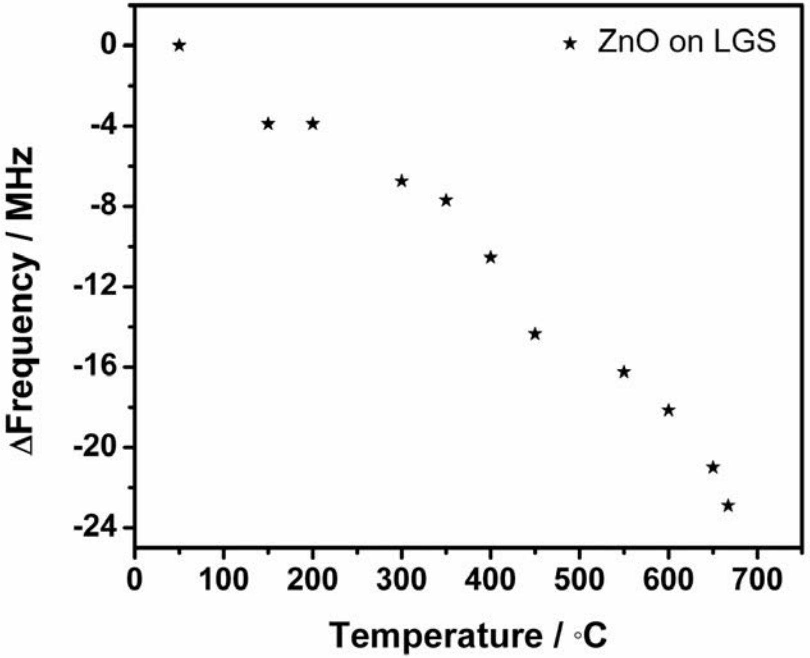
4. SAW sensor experiment setup

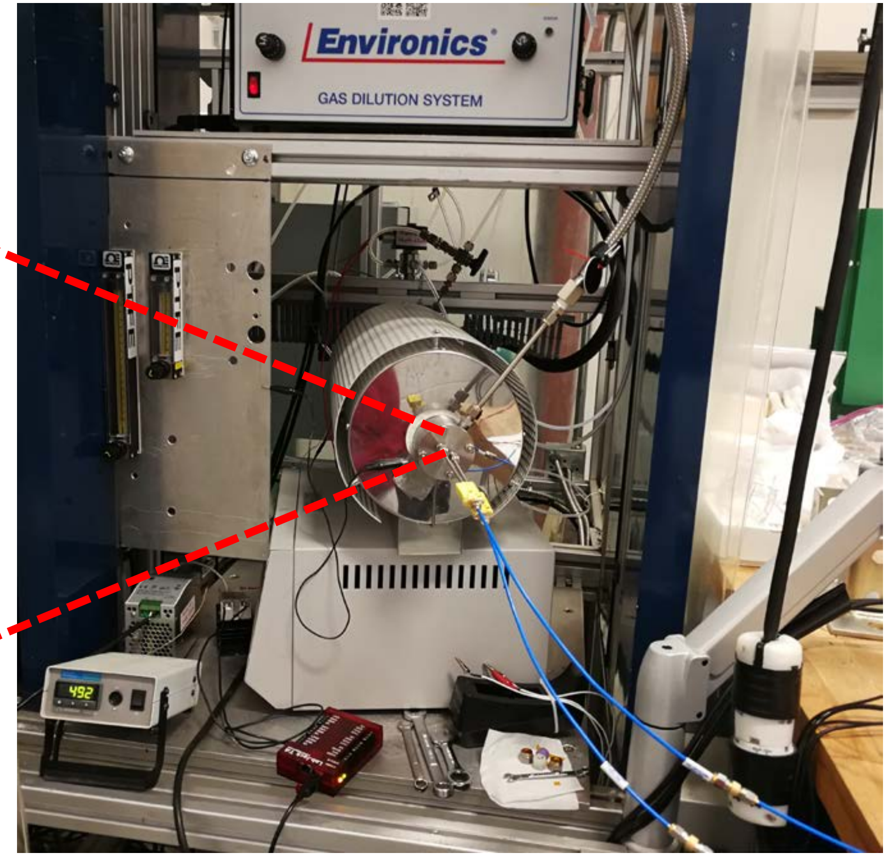




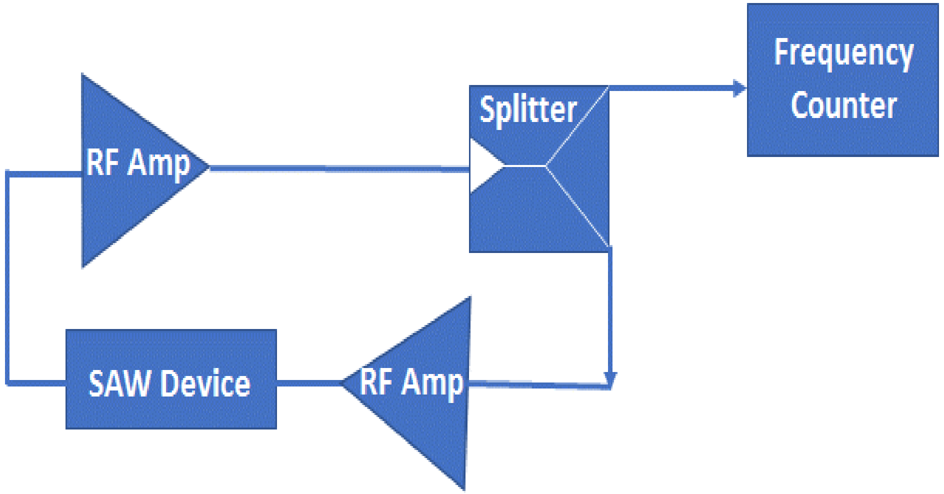
Resonant frequency change of the drop-cast ZnO nanorod based LGS SAW sensor as a function of temperature

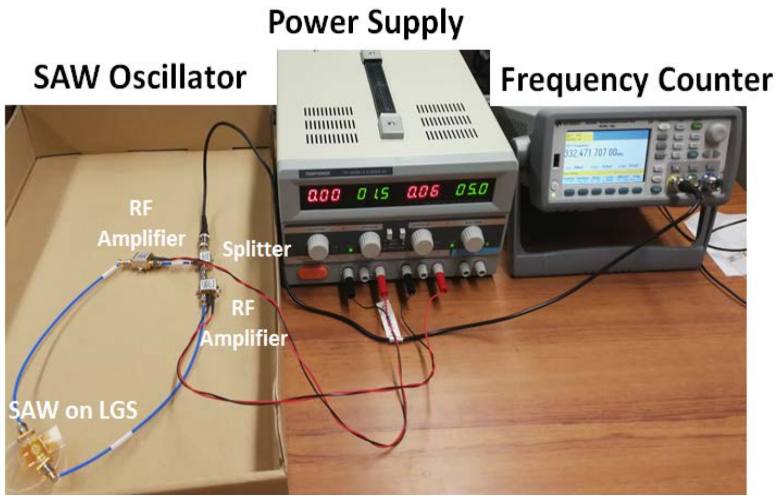
4. SAW sensor experiment setup

2nd generation
of test stage

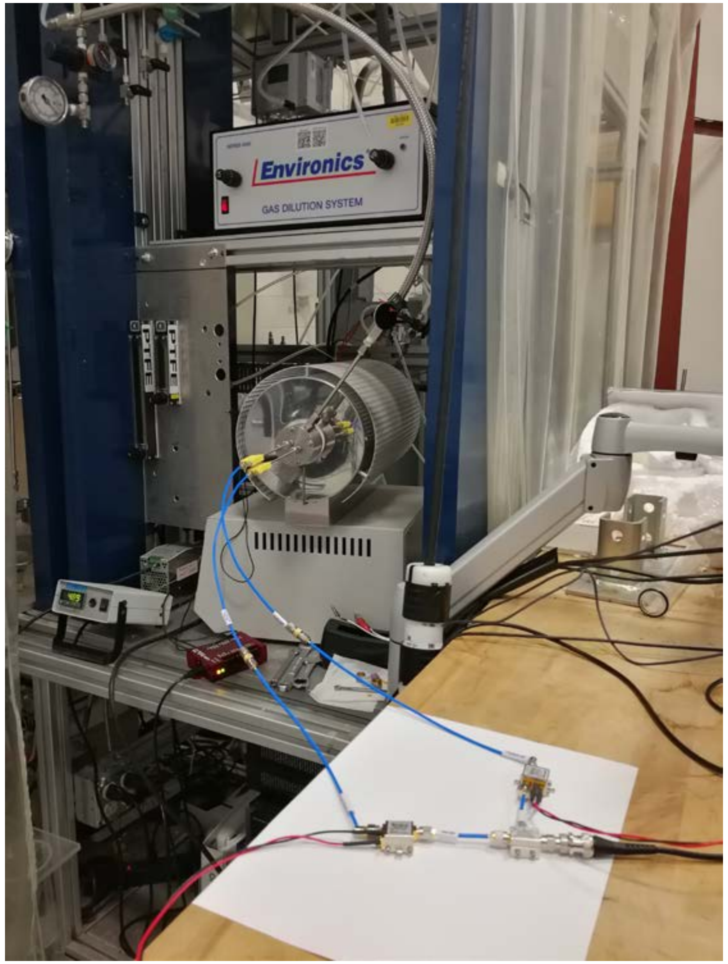


4. SAW sensor experiment setup





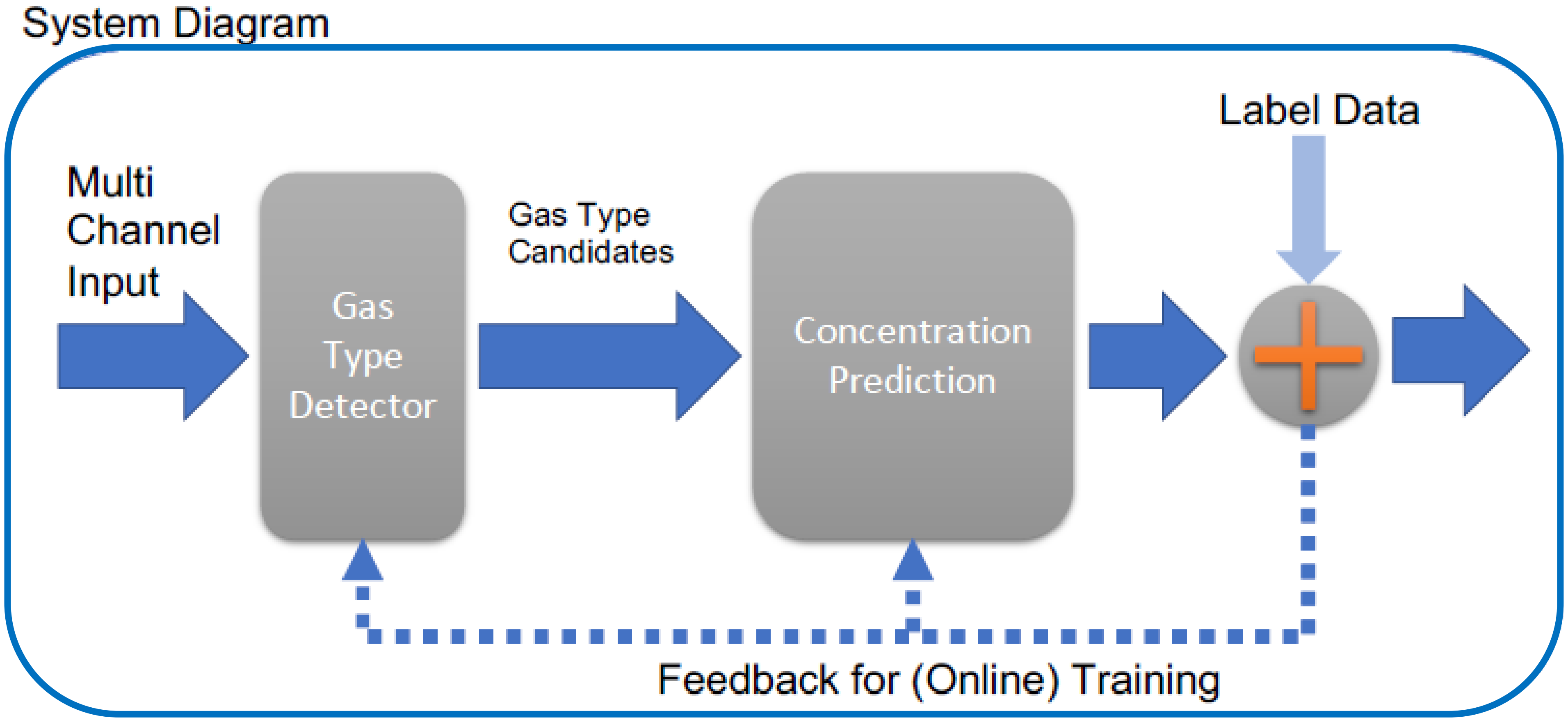
The experiment set-up for SAW oscillator circuit



5. Development of machine learning algorithms

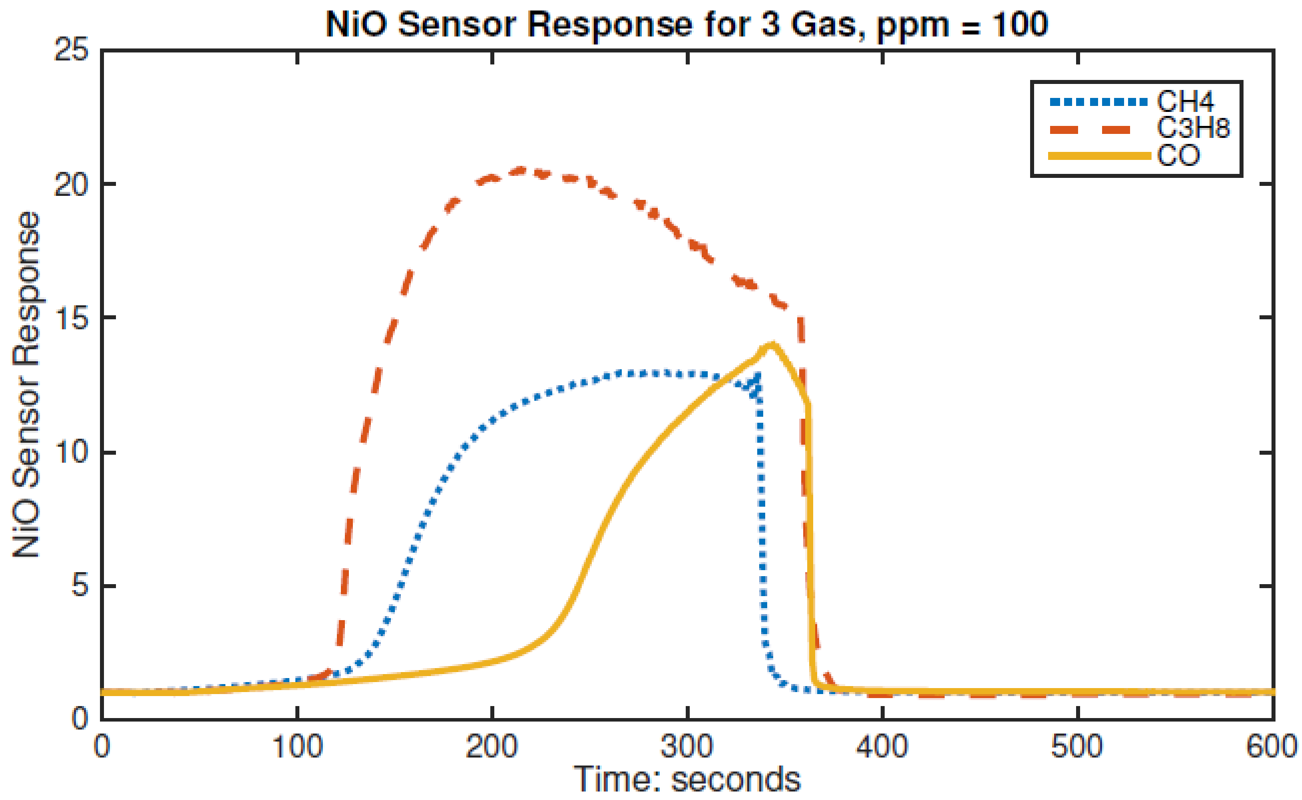
- Given large amount of field data, we could apply machine learning tasks for classification and regression problems. The latent feature behind the observation is difficult for human to extract, but the machine learning algorithms could identify those features via a variety of ways, e.g. space transform, de-noising, etc.
- Deep learning is also brought as a even more powerful tool, by taking advantage of neural network (NN) structures. Universal approximation theorem tells us a even single layer NN could approximate any smooth functions to arbitrary precision. Several types of NN are used in different areas, and some of them already achieves an accuracy of classification tasks higher than human beings.

5. Development of machine learning algorithms



The loop involves the training step if data and label are given. In the production phase, online learning algorithms can also be used for further training and refining each model.

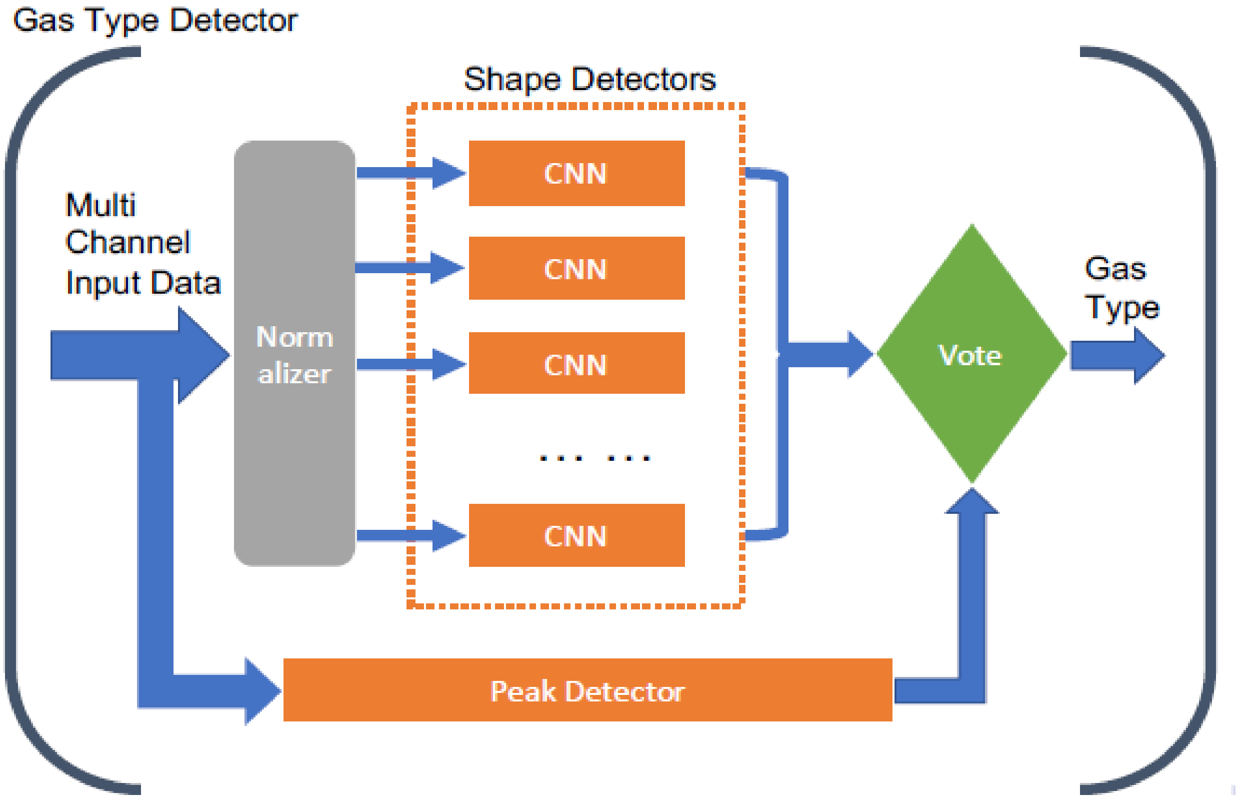
5. Development of machine learning algorithms



Different types of gases have their unique sensor response profile, the response amplitude and the response speed. Thus very different shapes of sensor response could be drawn for different types of gases.

Background and Project Update

5. Development of machine learning algorithms



Convolutional neural network (CNN) used to predict the gas species

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5. Development of machine learning algorithms

- Convolutional neural network (CNN) is more powerful than multi layer perception (MLP) but need more data input.
- Testing a simple version MLP due to limit data we have.
- MLP (50, 30, 20): 3 layers with 50, 30, 20 neurons in each layer, respectively.
- Using the sensing data from our previous CO, CH4 and C3H8 detection.
- Splitting data 4:1 for training and testing.

Model	SVM	MLP(50)	MLP(50,30)	MLP(50,30,20)	MLP(200,100,50)
Accuracy	0.798	0.910	0.911	0.917	0.920

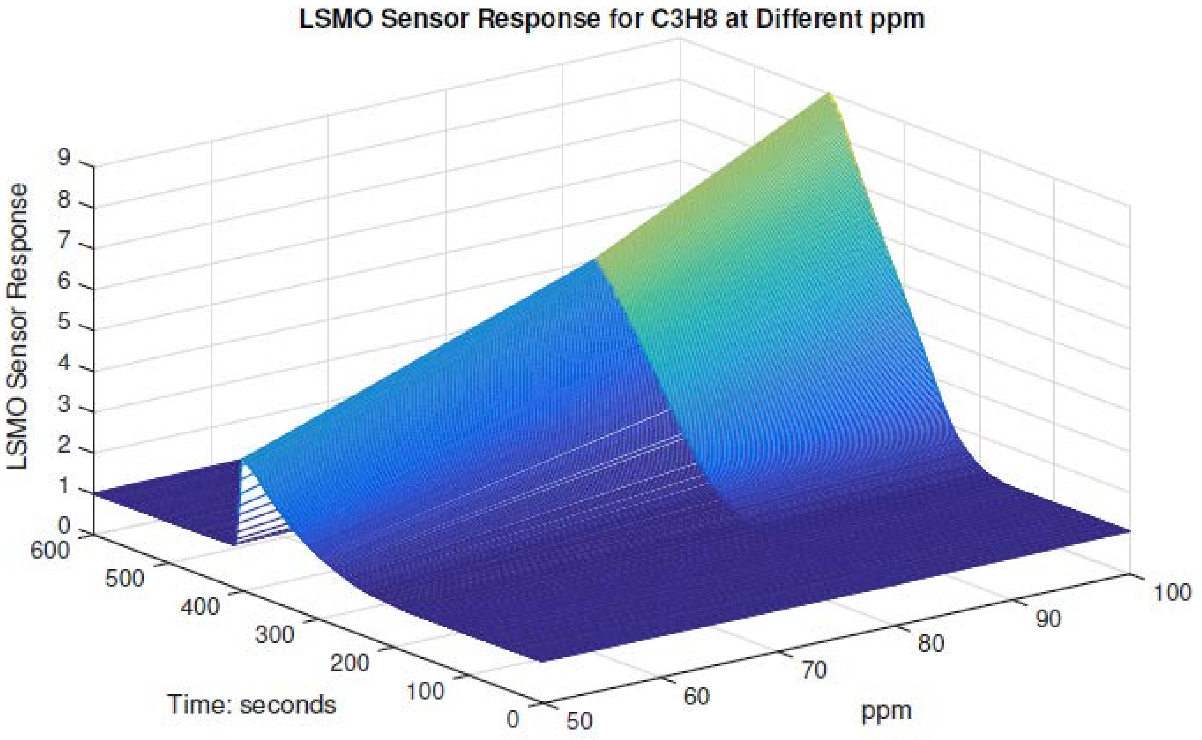
Table: SVM vs MLP (different number of layers)

SVM: support vector machine

Background and Project Update

5. Development of machine learning algorithms

- Gaussian Process Regression (GPR) used to predict the concentration.



The regression model tries to learn a surface that smoothly cover the training data points.

Preparing Project for Next Steps

Remaining Technological challenges

- Unstable frequency signal when operating under the configuration of SAW oscillatory circuit: We are making the new mask with bigger feature size (10 μm vs. 2 μm) – generating better signal.

Preparing Project for Next Steps

Market Benefits/Assessment

- Operating temperature >350 °C (e.g., 600 to 1000 °C)
- Stable sensing composites in the operating temperature range
- Passive and/or wireless sensing
- High sensitivity for various gases
- Identification of gas concentration and species in complicated combustion environment through machine learning

Technology-to-Market Path

- Build SAW oscillator circuit with stable frequency output using SAW device with larger feature size.
- Sensing test in NH_3, NO_2, CH_4 and O_2 at high temperature.
- Sensor stability test
- Identify industry collaborator with expertise in SAW oscillator design.

Concluding Remarks

- SAW device was fabricated on Langasite (LGS) wafer and Quartz.
- A second layer of photoresist was successfully deposited on SAW sensor to only expose the sensing area for selective decoration of sensing materials.
- Vertically aligned ZnO nanorods array were selectively and successfully grown on the sensing area through hydrothermal method, followed by removal of the 2nd photoresist layer using acetone.
- After hydrothermal growth and removal of the 2nd photoresist layer, some delamination of SAW circuit was observed. Drop-casting can solve this issue.
- SAW oscillator was developed for real-time monitoring. However, unstable frequency issue was encountered, which will be addressed using SAW circuit with larger feature size.
- Machine learning algorithms were developed.
- Also 5 Ph.D. students (Tony Kwak, Qiuchen Dong, Mingwan Zhang, Bo Zhang, and Xinyu Cai) are trained and involved in this project.

Acknowledgement

- Technician: Amehayesus Gebreyohannes in the Center for Nanoscale Systems at Harvard University
- Thank the supporting from Department of Energy and National Energy Technology Laboratory

Thank You