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


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# Objective & Vision

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

# Milestones

| Project Milestones | Verification method | Planned completion date | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Year1 | | | | Year 2 | | | | Year 3 | | | |
| | | Q1 | Q2 | Q3 | Q4 | Q1 | Q2 | Q3 | Q4 | Q1 | Q2 | Q3 | Q4 |
| **1. Complete the design of the circuit and pattern of passive wireless SAW arrays and also acquire commercial piezoelectric substrate Lanthanum Gallium Silicate (LGS)** | Include the design/blue-print generated by software and the picture of LGS in an upcoming quarterly report | | √ | | | | | | | | | | |
| **2. Successfully microfabricate at least six passive wireless SAW devices using commercial piezoelectric substrate Lanthanum Gallium Silicate (LGS)** | Include optical and SEM images of the as-fabricated passive wireless SAW on LGS in an upcoming quarterly report | | | | √ | | | | | | | | |
| **3. Achieve in-situ hydrothermal growth of 3D metal oxide nanorods on the active sensing area followed by perovskite nanosheath coating for at least three SAW sensors** | Include the SEM images of the as-fabricated 3D nanocomposite modified passive wireless SAW on LGS in an upcoming quarterly report | | | | | | √ | | | | | | |

# Milestones (Cont'd)

| Project Milestones | Verification method | Planned completion date | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Year1 | | | | Year 2 | | | | Year 3 | | | |
| | | Q1 | Q2 | Q3 | Q4 | Q1 | Q2 | Q3 | Q4 | Q1 | Q2 | Q3 | Q4 |
| **4. Complete the investigation of the structure, morphology, chemical, electronic structure, and thermal stability of metal oxide/perovskite core-sheath nanorod composite** | Include the characterization data (e.g., EDXS, TEM images, XRD and XPS spectra, thermal stability data, etc.) of the as-fabricated 3D nanocomposite in an upcoming quarterly report | | | | | | | √ | | | | | |
| **5. Achieve wireless detection using 3D nanord composite SAW sensor arrays with the wireless signal showing concentration-dependent behavior** | Include the real-time SAWs sensor's response data for CH4, O2, CO2, CO under the controlled lab environment in an upcoming quarterly report | | | | | | | | | √ | | | |
| **6. Develop machine learning algorithms to differentiate the concentration-dependent SAW signal from complicated gas mixture with more than 90% accuracy** | Include the developed machine learning algorithms with good accuracy in differentiating gases from SAW signals in an upcoming quarterly report | | | | | | | | | | √ | | |
| **7. Demonstrate the applicability of the wireless 3D nanorod composite SAW sensor arrays for monitoring methane combustion process in lab environment** | Include the sensing performance of the developed sensor for monitoring methane combustion as well as the gas concentration predicting by the developed machine learning algorithms in the final report | | | | | | | | | | | | √ |

# Outline

- Background
- Results and Discussions
- Accomplishments & Summaries
- Future work

# *Background*

## Importance of Harsh Environment Gas Sensors

### 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

**FUEL COSTS**
$39 Million/Year ➡

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
- $4.1 million for entire installed fossil capacity

**>600**

### Value Derived for an Existing Coal Fired Power Plant

➡ **Gaseous Emissions**

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

➡ **Solid Wastes**

➢ **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

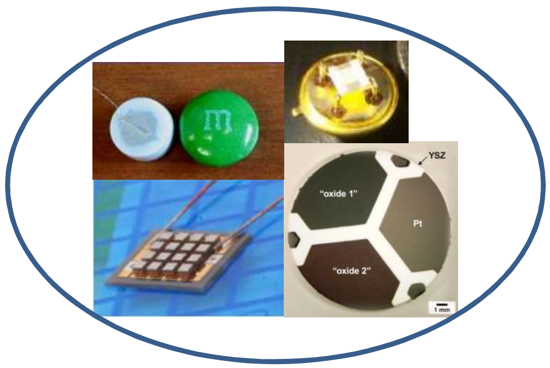
# *Background*

## *Sensors for harsh environments*

**Solid Oxide Fuel Cells**
- 650 – 1000 °C
- Atmospheric pressure

**Advanced Combustion Turbines**
- Up to 1300 °C combustion temperatures
- Pressure ratios of 30:1

**Automotive Engine**
- up to 1000 °C
- Compression ratio ~10:1




**Ultra Supercritical Boilers**
- Up to 760 °C temperature
- Up to 5000 PSI pressure

**Gasifiers**
- Up to 1600 °C, and 1000 PSI (slagging gasifiers)
- Erosive, corrosive, highly reducing environment

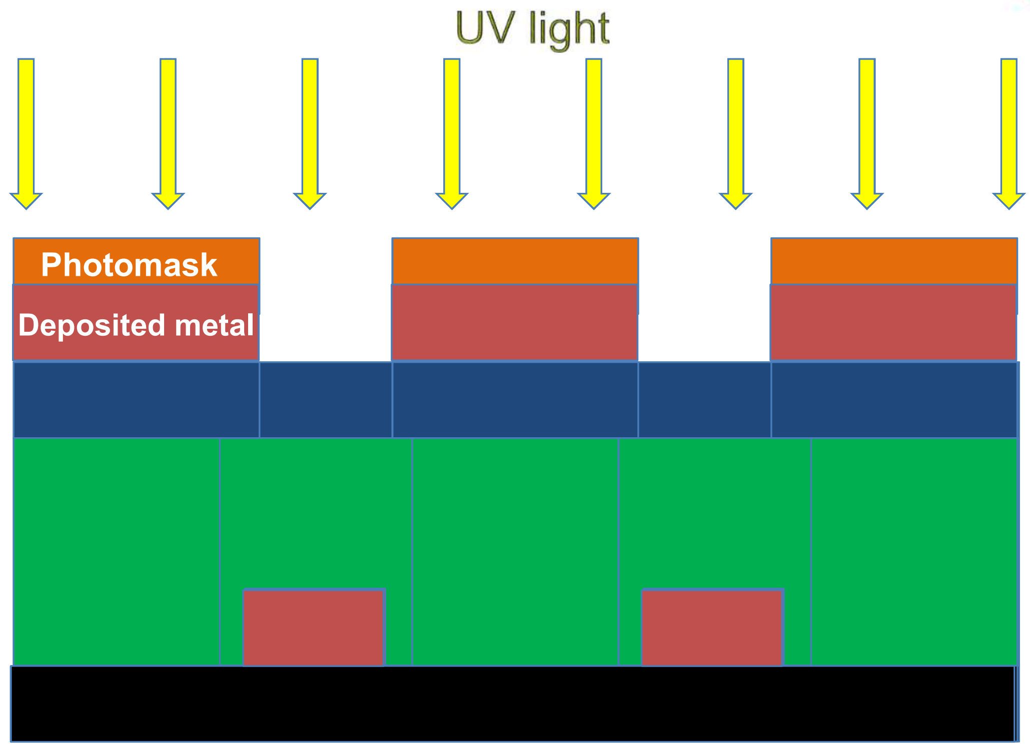
# *Research Objectives*

1. To fabricate SAW sensor arrays on high-temperature stable LGS wafer
2. To selectively grow metal oxides nanowires (coated with high-temperature stable perovskites) in the sensing area of SAW device
3. To improve selectivity through machine learning algorithms

# 1. Fabrication of SAW sensor arrays on high-temperature stable LGS wafer (Lift-off photoresist processing)

- 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

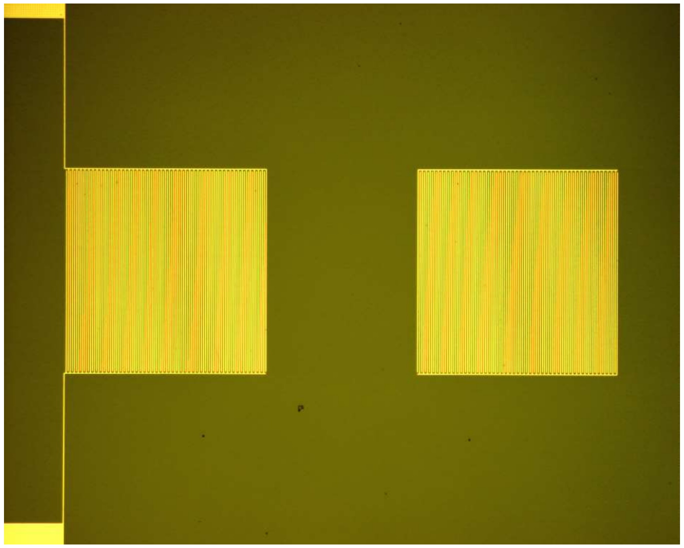
** Minimum feature size: 2 µm*

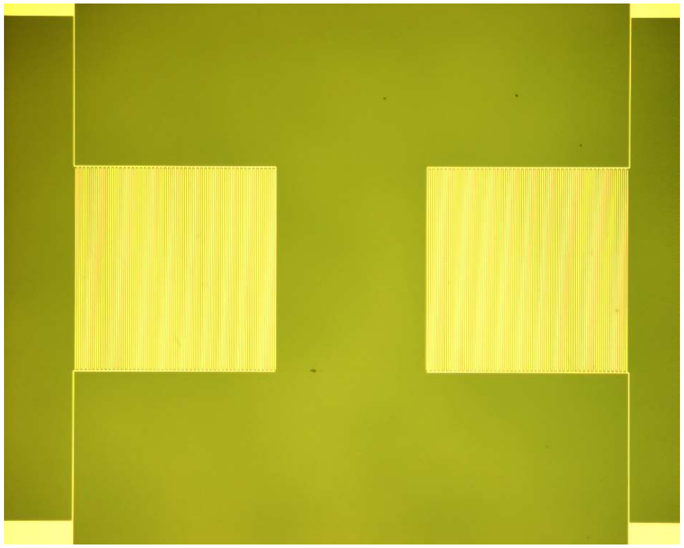



**The general lift-off process (positive)**

# 1. Fabrication of SAW sensor arrays on high-temperature stable LGS wafer (Lift-off photoresist processing) (Cont'd)

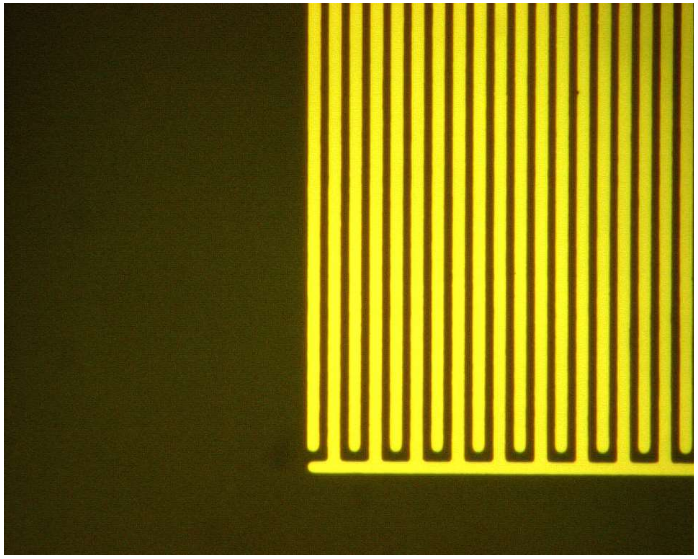
- SAW circuits on LGS after lift-off on LGS.

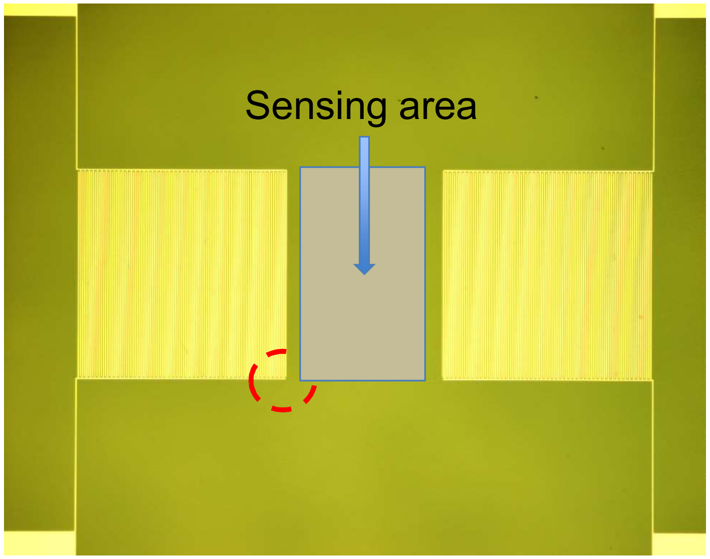




# 1. Fabrication of SAW sensor arrays on high-temperature stable LGS wafer (Lift-off photoresist processing) (Cont'd)

- SAW circuits on LGS after lift-off on LGS.

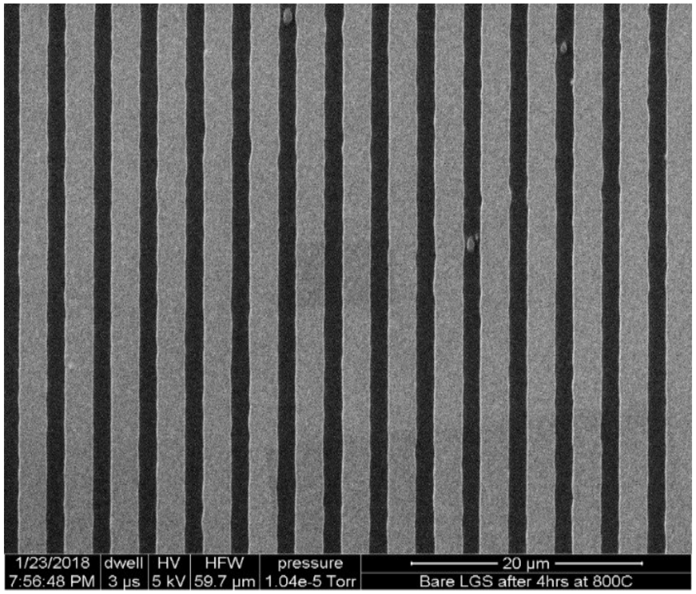


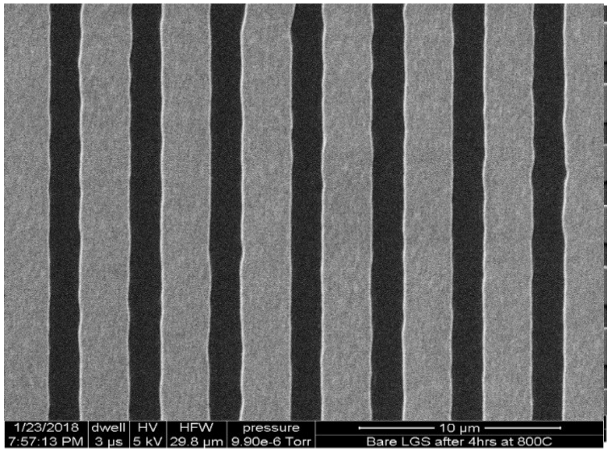


# *1. Fabrication of SAW sensor arrays on high-temperature stable LGS wafer (Lift-off photoresist processing) (Cont'd)*

- Study the thermal stability of the SAW circuits.

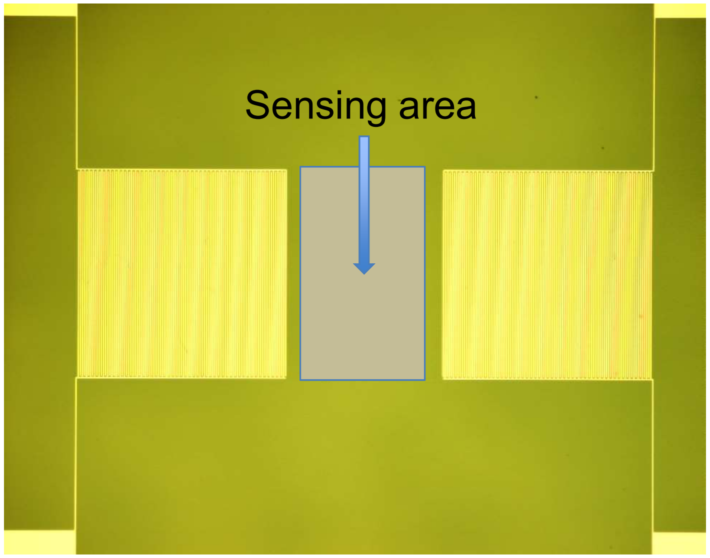
After thermal treatment (4 hrs at 800 °C under air atmosphere)



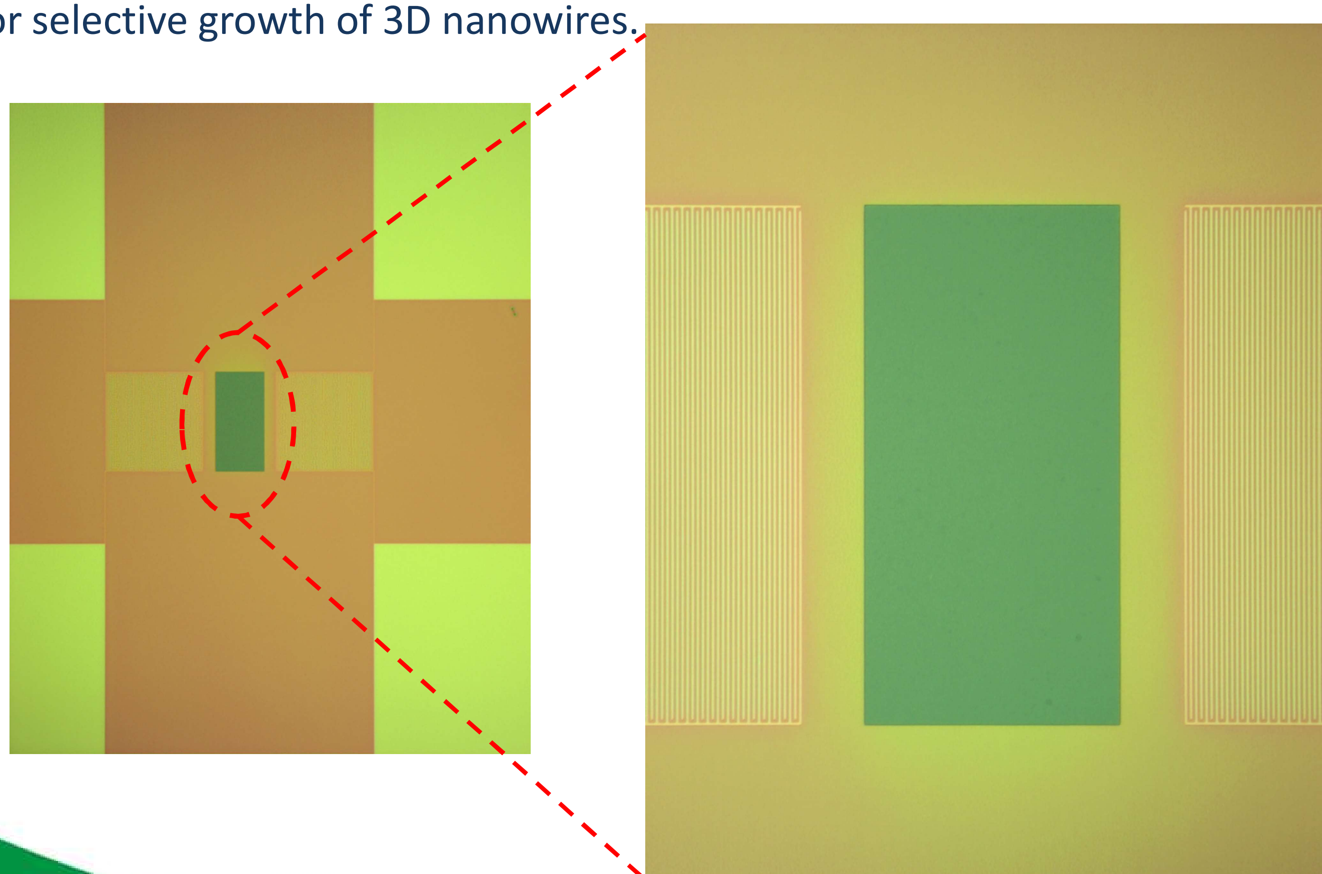
# 1. Fabrication of SAW sensor arrays on high-temperature stable LGS wafer (Lift-off photoresist processing) (Cont'd)

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



# *1. Fabrication of SAW sensor arrays on high-temperature stable LGS wafer (Lift-off photoresist processing) (Cont'd)*

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

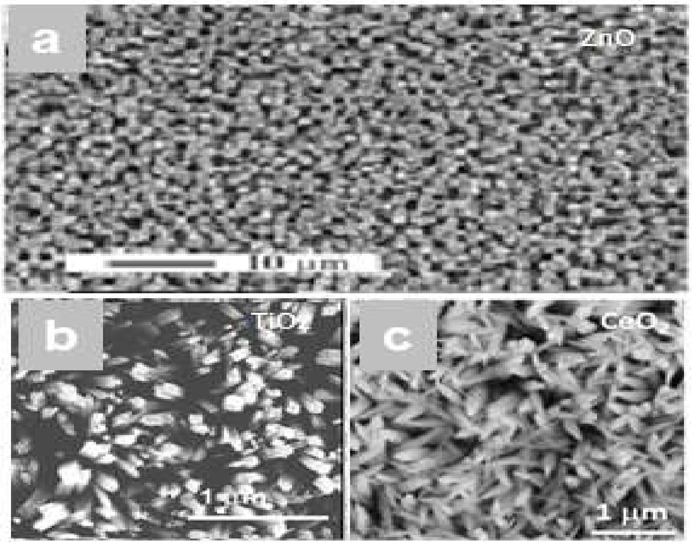


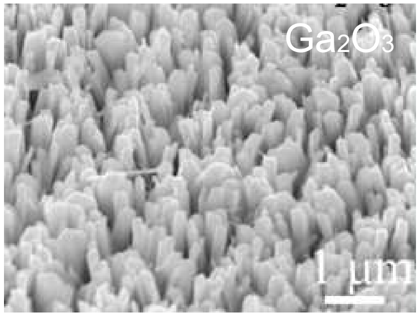
# 2. Hydrothermal growth of vertically aligned metal oxides nanorods

## Why hydrothermal method?

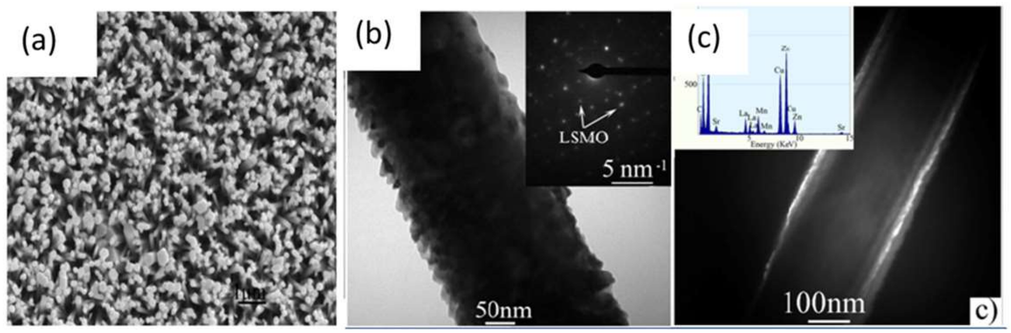
- Vapor-phase-transport method and sol-gel method have been developed to synthesize 3D metal oxide nanostructures, their application to large scale production of 3D arrays are greatly limited due to the low reproducibility, high-cost, and/or complicated procedures.
- Hydrothermal method has emerged lately 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 team, such as $CeO_2$, ZnO, $TiO_2$, etc.

# 2. Hydrothermal growth of vertically aligned metal oxides nanorods (Cont'd)

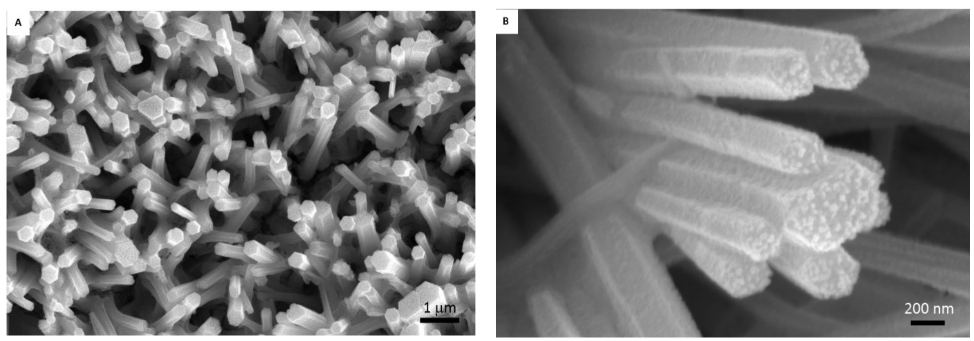


# 2. Hydrothermal growth of vertically aligned metal oxides nanorods (Cont'd)




LSMO on ZnO nanorods

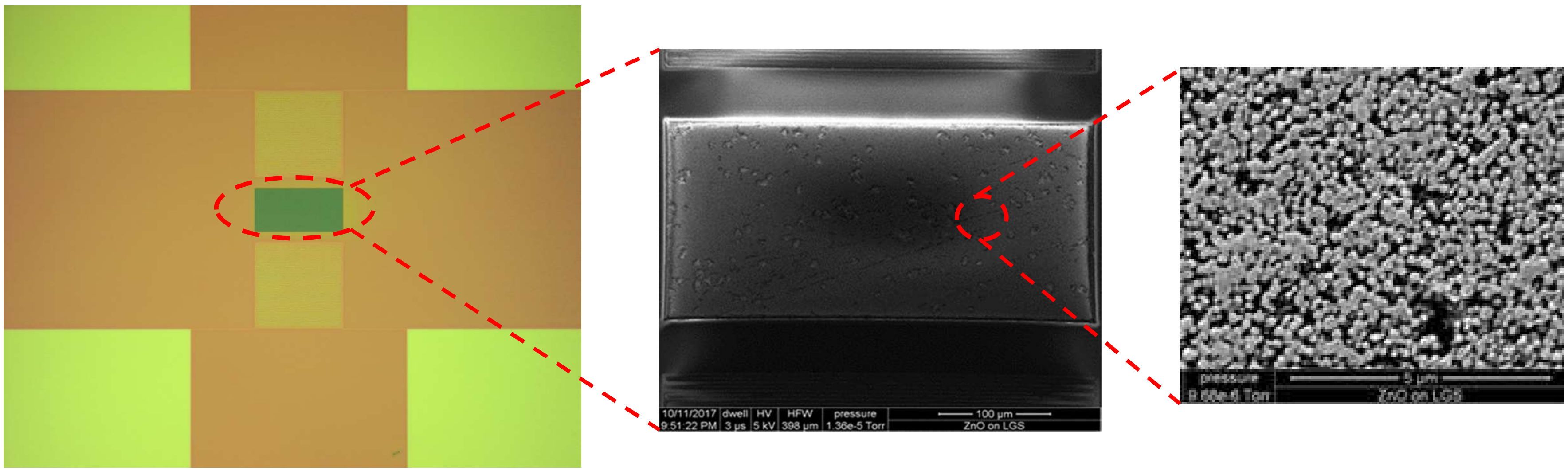



LSCO on ZnO nanorods

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

# *3. Selective growth of vertically aligned metal oxides nanorods on the sensing area of SAW device on LGS*

Precursors (Zinc nitrate + Hexamethylenetetramine) at ~95 °C for 6~8 hrs




**We selectively grew vertically aligned metal oxides on the sensing area!**

# 3. Selective growth of vertically aligned metal oxides nanorods on the sensing area of SAW device on LGS

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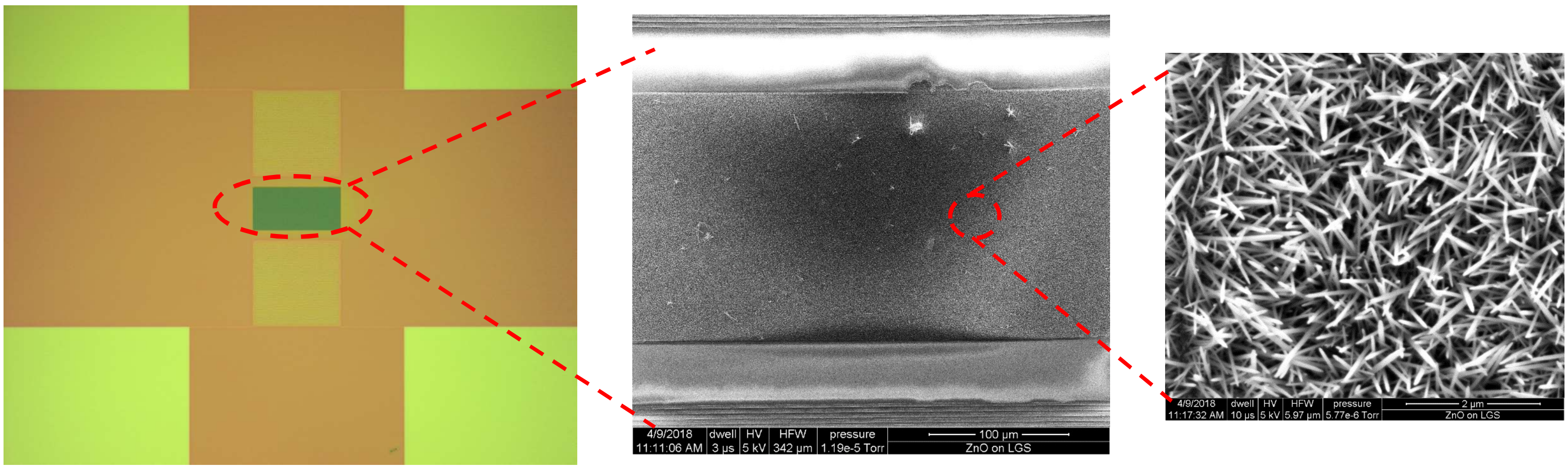
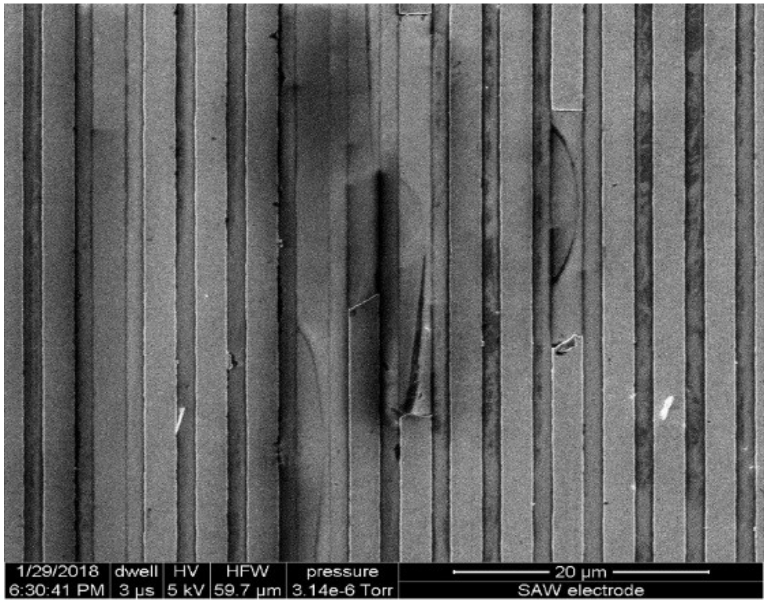



**We selectively grew vertically aligned metal oxides on the sensing area!**

# *3. Selective growth of vertically aligned metal oxides nanorods on the sensing area of SAW device on LGS (Cont'd)*

Challenge we are facing

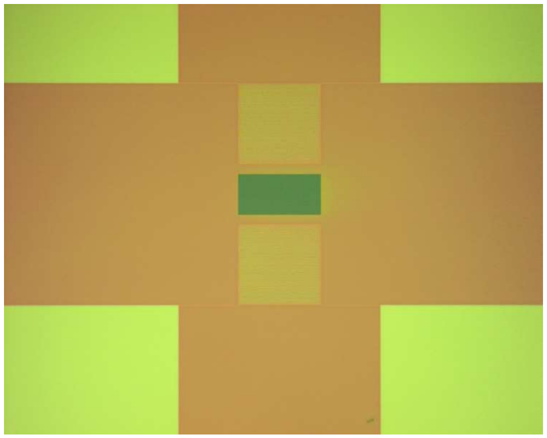



**Trouble-shooting**

- During device fabrication, the dehydration temperature was increased from 180 °C to 200 °C to remove water molecules on the surface of LGS substrate.
- The time of the dehydration step was prolonged from 5 to 30 minutes for the same purpose.
- The sonication cleaning of the LGS substrate in two different solvents (Acetone and Isopropanol), was conducted for 10 minutes each before the spin coating of primer to eliminate any contaminants (or dusts) on the surface of the LGS substrate.

**None of above strategies worked to alleviate the delamination!!!**

# *3. Selective growth of vertically aligned metal oxides nanorods on the sensing area of SAW device on LGS (Cont'd)*



**Trouble-shooting**

- Contacting the LGS supplier/manufacturer (SICCAS/AXTAL): the supplier of our LGS wafers experienced a similar issue.
- Their suggestion is to use a liquid detergent for cleaning up the surface of LGS substrate before conventional fabrication process.
- According to the discussion with LGS wafer supplier, soaking the LGS substrate into the detergent might help removing the remained oil molecules on the surface since the oil is normally used during their wafer polishing step
- We did, but not work either.

**Two LGS suppliers in the world:**

- Shanghai SICCAS High Technology Corporation, P.R. China (AXTAL, Germany, is the Branch of this Chinese company)
- Fomos-Materials, Russia

## Summaries

- A complete lift-off process has been conducted and shown success in SAW device fabrication on Langasite (LGS) wafer.
- A second layer of photoresist was successfully deposited on SAW sensor to only expose the sensing area for selective growth of metal oxide nanorods arrays.
- Vertically aligned ZnO nanorods array were selectively and successfully grown on the sensing area through hydrothermal method, followed by removal of the 2$^{nd}$ photoresist layer using acetone.
- After hydrothermal growth and removal of the 2$^{nd}$ photoresist layer, some delamination of SAW circuit was observed.
- Also 4 Ph.D. students (Tony Kwak, Qiuchen Dong, Mingwan Zhang and Bo Zhang) are involved in this projects.

# *Future work*

- To fabricate SAW sensor arrays on LGS wafers from a different supplier to see if the delamination after hydrothermal growth could be alleviated.
- To collect the ZnO nanorods (with or without perovskite coating) and re-suspend them in water for drop-deposition in the sensing area as an alternative way.
- To develop machine learning algorithms to differentiate the concentration-dependent SAW signal from complicated gas mixture with more than 90% accuracy.

# *Acknowledgement*


- Collaborators: Professors Pu-Xian Gao and Sanguthevar Rajasekaran at University of Connecticut
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# Thank You

## Questions?