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

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NETL Crosscutting meeting

3/20/2017

FE0026219

9/1/2015 ~ 8/31/2018

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Objective & Vision

- Projective Objective:
- The project objective is to develop a new class of wireless 3D nanorod composite arrays based high temperature surface-acoustic-wave gas sensors for selective and reliable detection through machine learning algorithms

- Our Strategy:
- 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
- Device Fabrication
- Results
- Sensing material deposition
- Accomplishments & Summaries
- Future work

Background

Why are gas sensors for harsh environment critical?

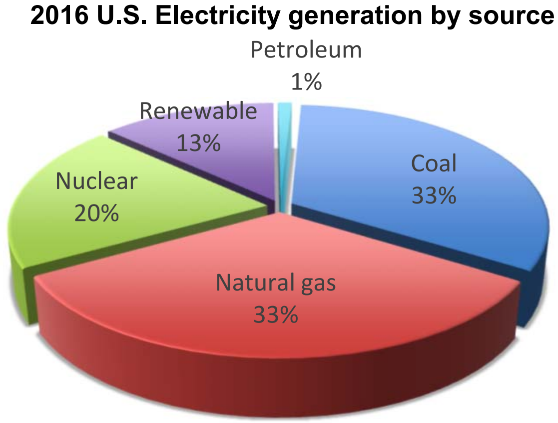
- Safety, Environment and Economy

I. **Detection** of fuel leaks in jet engines

II. **Emission control** → Increase fuel efficiency & Reduce environmental pollution.

III. **Positive impact** on the economy

2016 U.S. Electricity generation by source



1% Improvements/increases are easily achievable
by advanced sensors and controls.

Coal Consumed
35,700 MMBTU/yr
$70 Million/yr
@ $2/MMBTU

Power Generated
3.5 Billion kWh/yr
@ 80% capacity factor

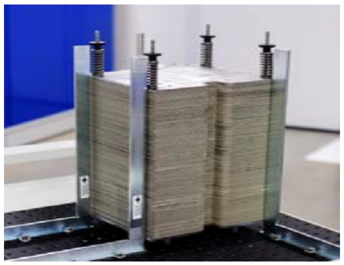
Entire Coal-fired fleet

- 1% Efficiency improvement
- $300 million coal cost savings
- Reduction of 14.5 million metric tons CO_2 per year

*** NETL Sensors and Controls Program Overview, 2012.**

Background

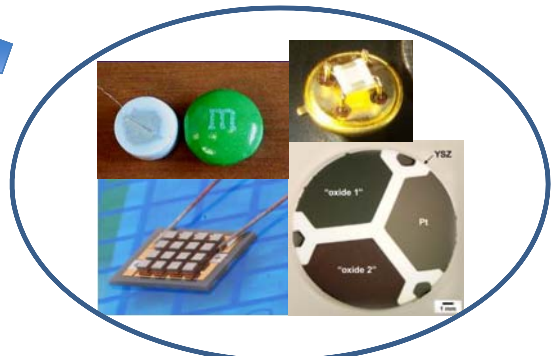
Sensors for harsh environments



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

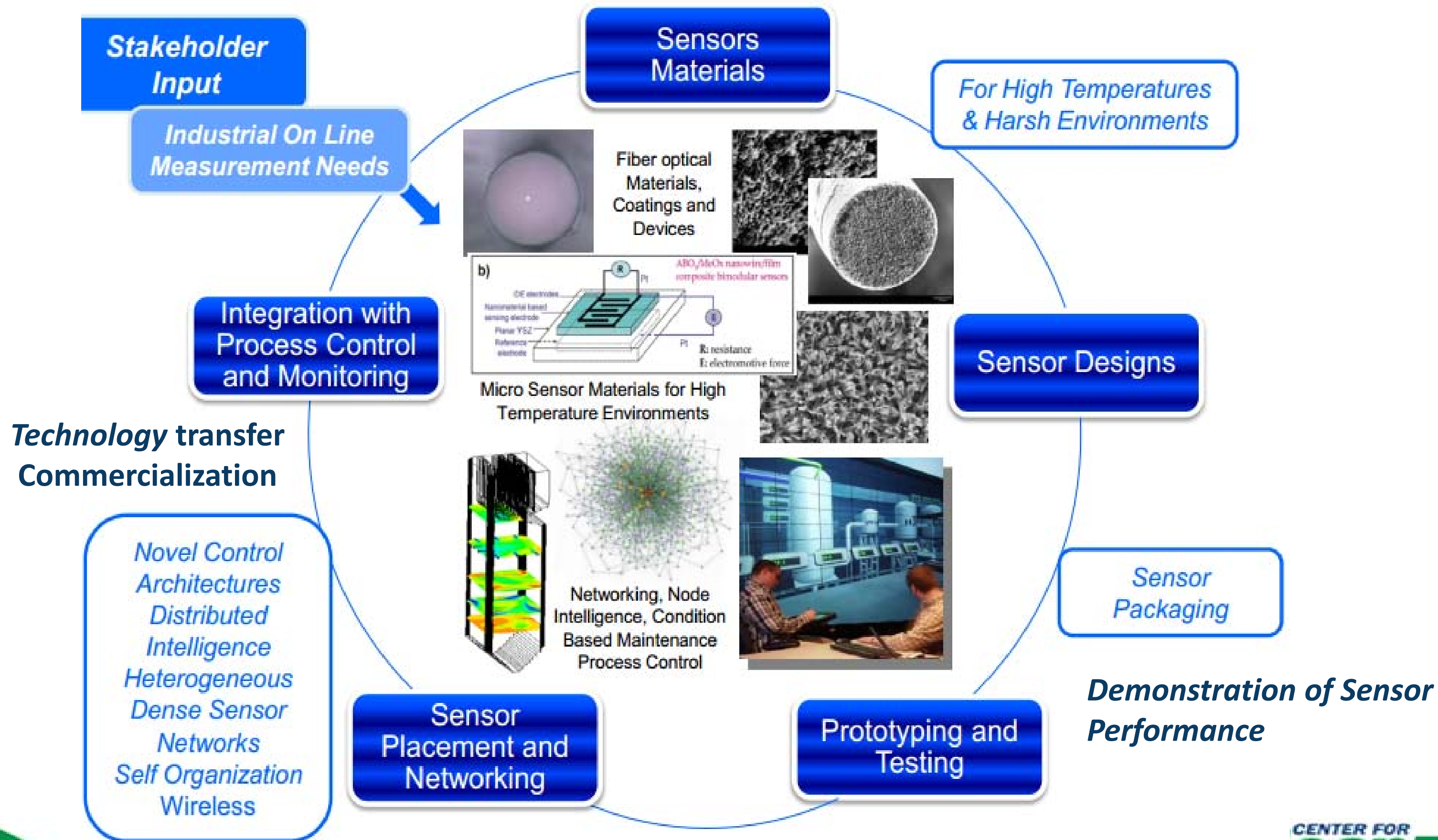


Gasifiers
- Up to 1600 °C, and 1000 PSI (slagging gasifiers)
- Erosive, corrosive, highly reducing environment

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

Background

Research in controls and sensors

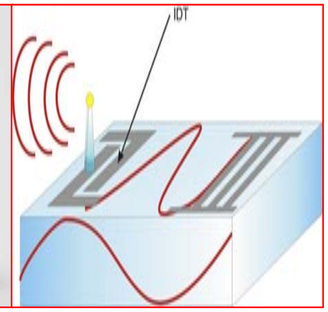


* NETL Sensors and Controls Program Overview, 2012.

Background

Applications of Surface Acoustic Wave (SAW) sensor

SAW sensor



Inherent Functionality

- Pressure
- Temperature
- Strain
- Mass
- Torque

Additional Functionality

- Chemical Vapors
- Humidity
- Ultraviolet Radiation
- Biological Matter
- Magnetic Fields

Other Application

- Personalized Health Care
- Intelligent Transportation Systems

URL; http://industrial.embedded-computing.com/article-id/?3803=.

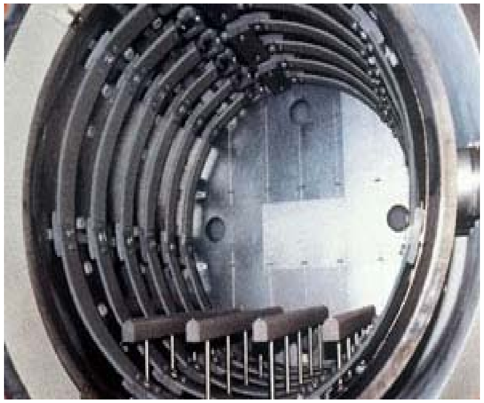
Background

Applications of SAW sensor for harsh environments

High temperature furnace

High pressure chamber

Jet turbine



URL; https://www.wired.com/2013/07/diy-spacesuit-testing-and-planning/, http://www.explainthatstuff.com/jetengine.html, https://www.elmettechnologies.com/products/tungsten-molybdenum-hot-zones/.

Background

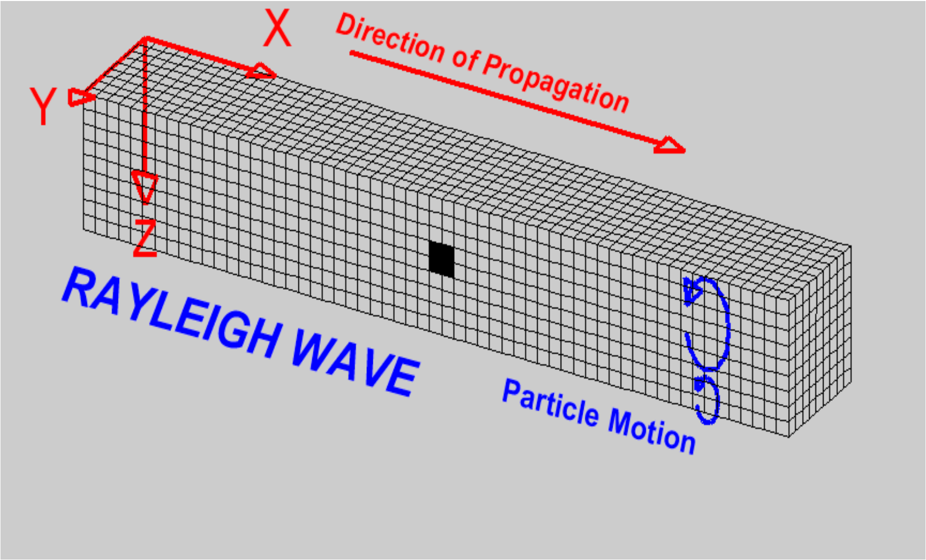
Why Surface Acoustic Wave (SAW) gas sensor?

- Recently, 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 absorption and 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, langasite has been intensively investigated for high temperature SAW-based gas 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

Principle of SAW sensor

- In 1885, Lord Rayleigh introduced the concept of surface acoustic waves, also known as Rayleigh waves
- All acoustic wave devices make use of the piezoelectric effect to transduce electric signals into mechanical(Rayleigh) waves and vice versa
- The piezoelectric effect occurs only in anisotropic crystalline materials since isotropic (symmetrical) crystalline materials show the zero net spontaneous charge distribution in a unit cell



URL; http://www.geo.mtu.edu/UPSeis/waves.html

Background

Critical characteristics of the piezoelectric material as a SAW sensor substrate

- Mechanical Strain (ε)

A dimensionless property describing the changes in length of a material

$$\varepsilon = S\sigma = \frac{the\ length\ under\ stress}{the\ length\ without\ stress}$$

- Electromechanical Coupling Factor (k)

The efficiency of the transduction of the piezoelectric material between mechanical and electrical energy and vice-versa

$$k = \sqrt{\frac{mechanical\ energy\ stored}{electric\ energy\ applied}} = \sqrt{\frac{electrical\ energy\ stored}{mechanical\ energy\ applied}}$$

- Piezoelectric charge constant (d)

$$P = d\sigma + \varepsilon_\sigma E$$
$$\varepsilon = dE + SE\sigma$$

$$P = d\sigma$$
$$\varepsilon = dE$$

$$k = d^2\sqrt{S^E\varepsilon_\sigma}$$

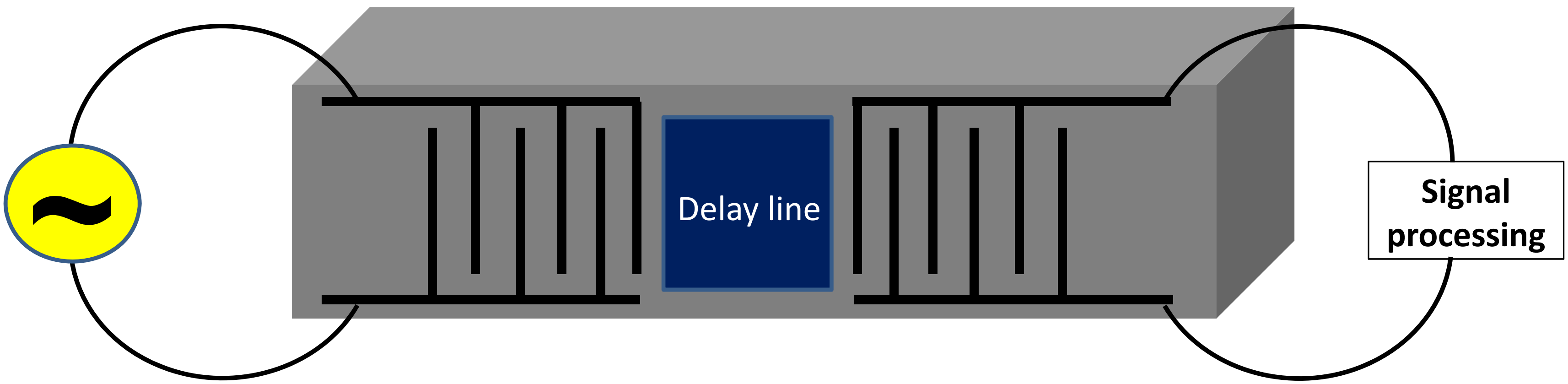
σ:Stress
P: Polarity
E: Electric field
S: Compliance

When the external electric field is zero, the polarization is proportional to the d and the σ. On the other hand, when it comes to the zero stress applied, the strain is proportional to the d and the E.

- To obtain the maximum efficiency, a high d is required
- For a given d, a large compliance and large permittivity will increase the k

Background

Operation of wired SAW sensor



A sinusoidal electric signal (AC) is sent through the input interdigital electrode (IDT) → The array of IDT alternates polarity because of the electrical signal → Create alternating regions of electric fields between fingers

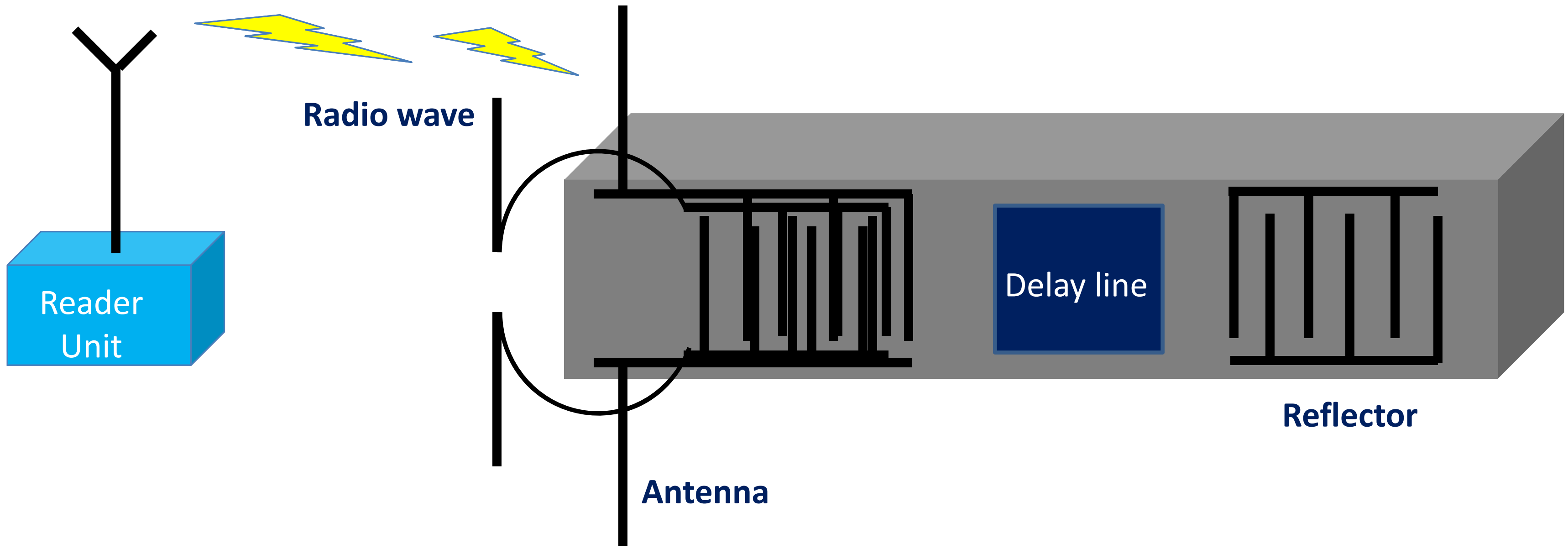
→ The electric fields lead to alternating regions of tensile and compressive strain between fingers of electrodes → Produce a mechanical wave at the surface

→ The acoustic wave reaches the output IDT and generates an electric field varying along the length of the substrate

→ Process changes in the output signal from the original signal

Background

Operation of wireless SAW sensor



The reader unit sending a radio frequency (RF) electromagnetic read-out signal → The antenna picking up the read-out signal → The received signal converted into a SAW signal by the converse piezoelectric effect

→ The SAW propagates and is reflected by the reflector

→ The returning SAW re-converted into electrical signals by the IDT and retransmitted to the reader unit

Device Fabrication (Photolithography)

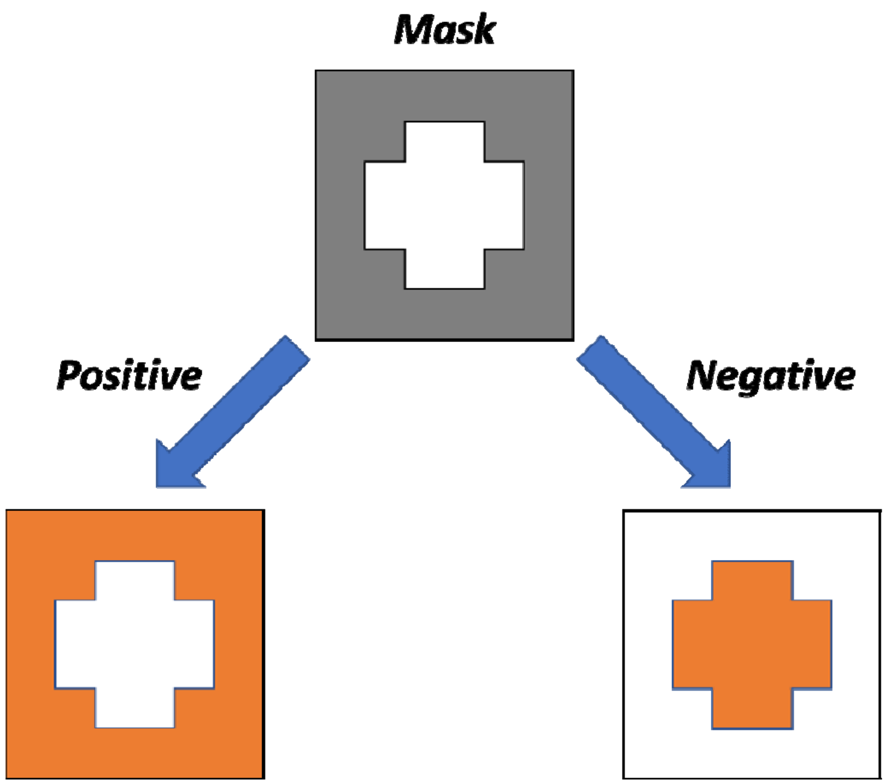
- Using a light sensitive material to fabricate specific patterns on a substrate

- Basic steps
  1. Cleaning
  2. Photoresist coating
  3. Light exposure
  4. developing

- Resolution

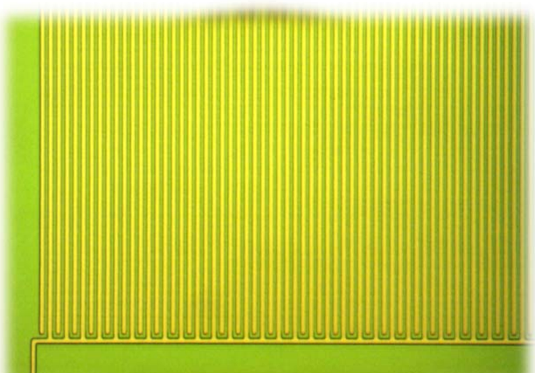
$$p_{min} = 1.5[\lambda(g + 0.5d)]^{1/2}$$

- p_{min}; the minimum feature size
- λ; the exposure wavelength
- g; the gap between the mask and the resist
- d; the thickness of the resist

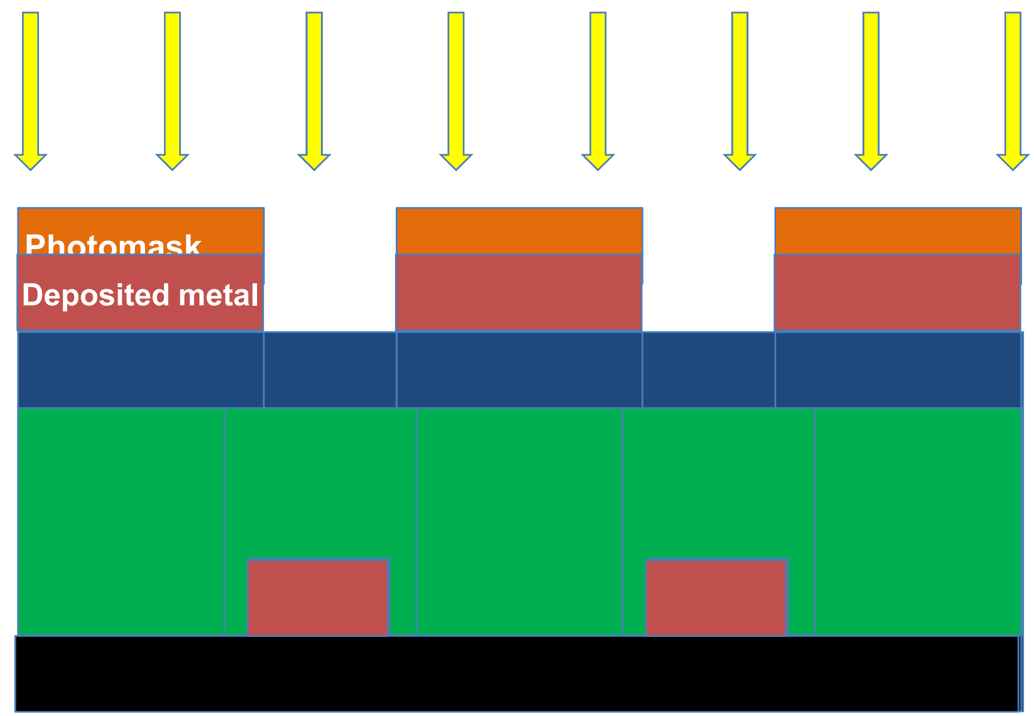


Device Fabrication (Lift-off photoresist processing)

- 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

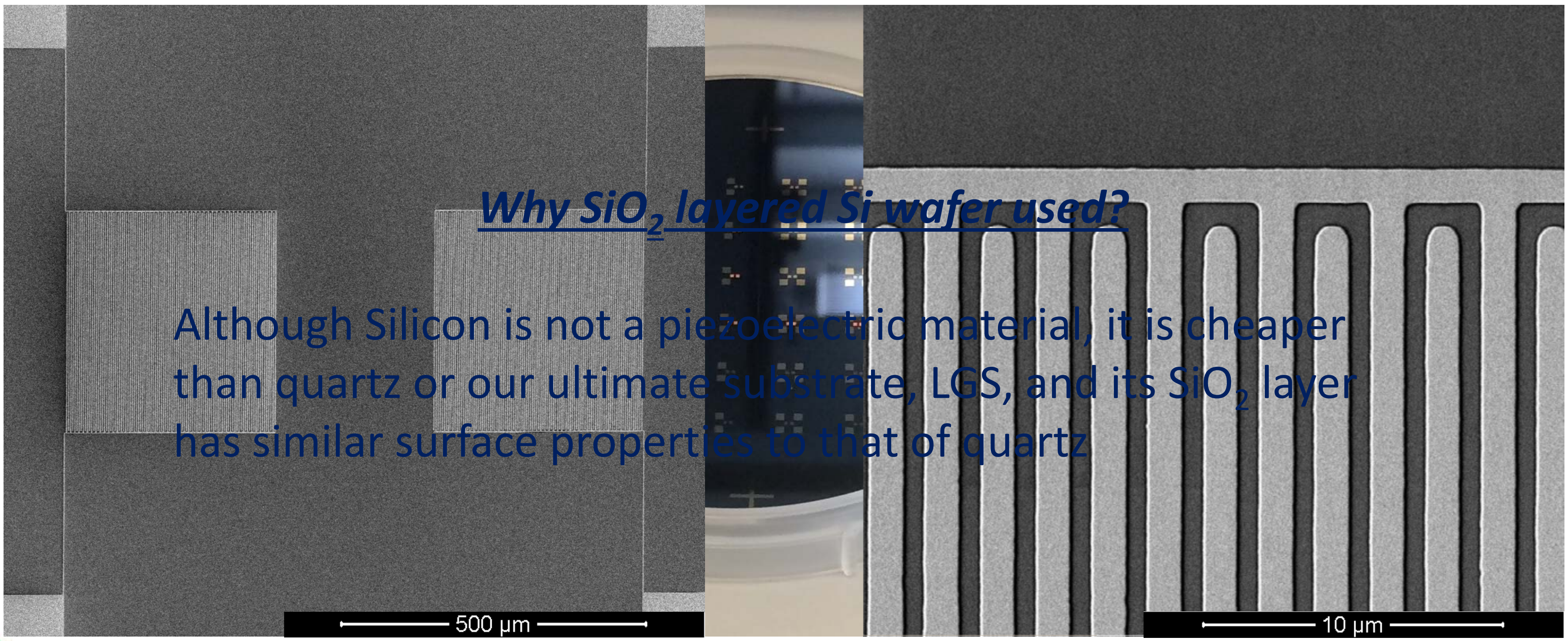


** Minimum feature size: 2 μm*



The general lift-off process (positive)

Results (The lift-off process on SiO_2 layered Si wafer)



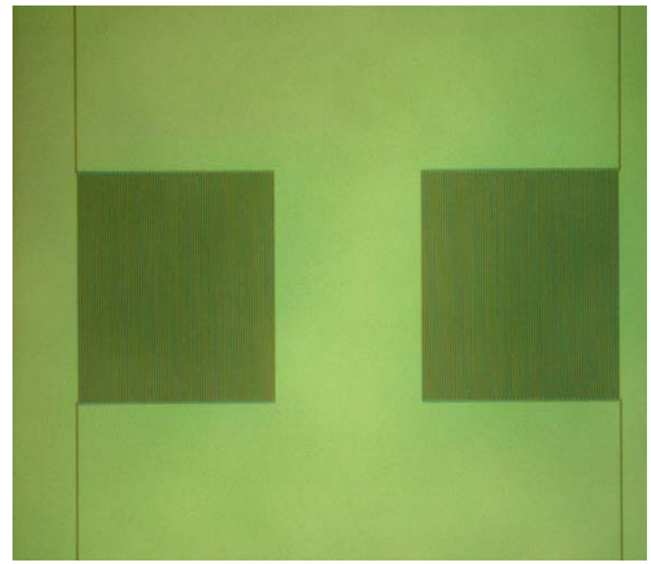
Why SiO_2 layered Si wafer used?

Although Silicon is not a piezoelectric material, it is cheaper than quartz or our ultimate substrate, LGS, and its SiO_2 layer has similar surface properties to that of quartz

Pt/Ti deposited on SiO_2 layered Si wafer

Results (Trouble shooting in Quartz fabrication)

- Collapsed features found in almost all areas on the surface although the optimized parameters for SiO_2 layered Si wafer were applied
- To address the issue, HMDS (Hexamethyldisilazane) was introduced so that it forms bonds with surface and produces a polar (electrostatic) surface to isolate moisture adhesion on wafer surface



First attempt on Quartz / After HMDS treated

Increase the adhesion between wafer and photoresist coating layer

*

	Surface tension (dyne/cm)	H_2O on surface (molecule/um^2)
Pre-HMDS	78	>35
Post-HMDS	21	<1

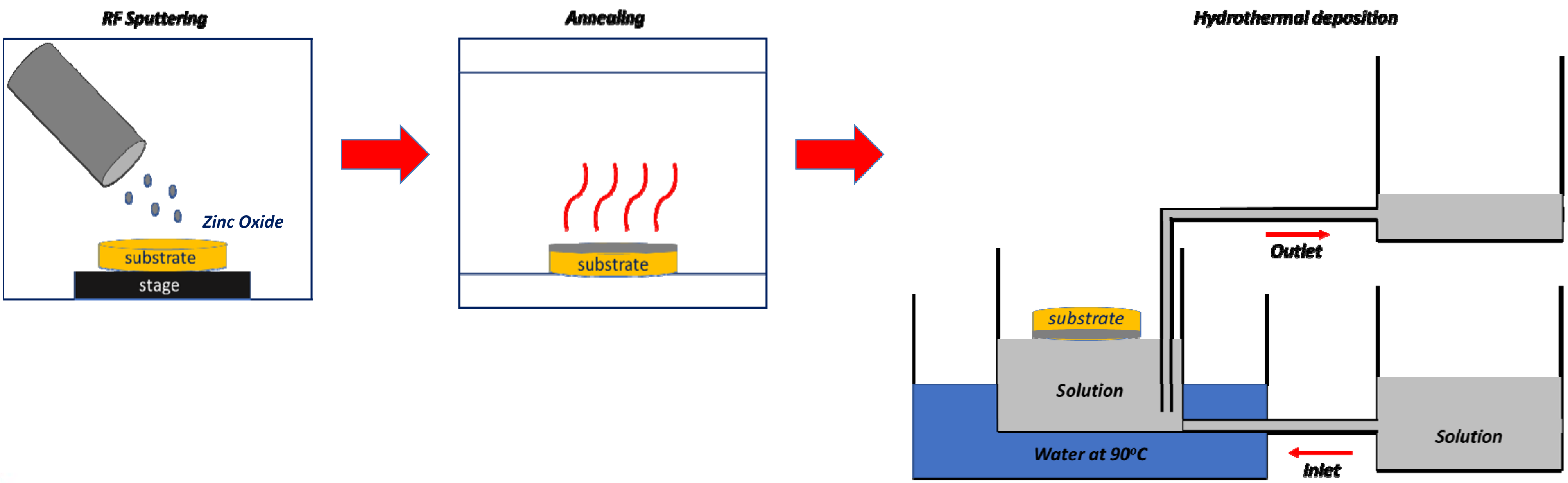
**J. Deng, Introduction to photolithography, Center for nanoscale system, Harvard, 2009*

Sensing material deposition (Hydrothermal method)

Why hydrothermal method for vertically aligned metal oxide nanorod arrays?

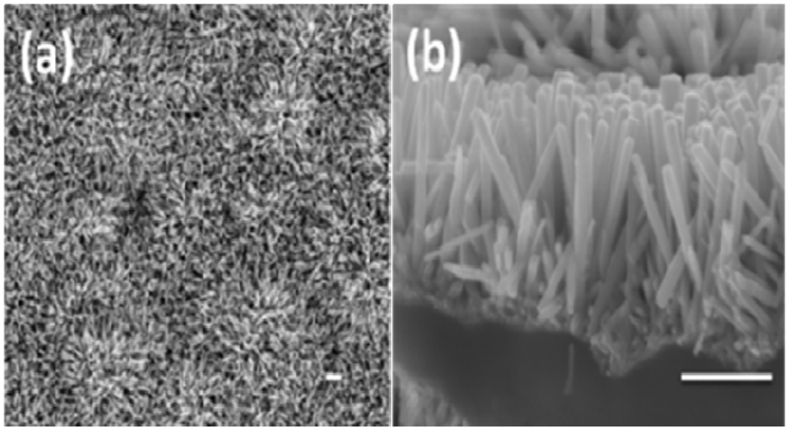
- Vapor-phase-transport method and sol-gel method have been developed to synthesize 3D metal oxide nanostructures, their application to large scale production of 3D arrays are greatly limited due to the low reproducibility, high-cost, and/or complicated procedures.
- Hydrothermal method has emerged lately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

Sensing material deposition (Hydrothermal method)

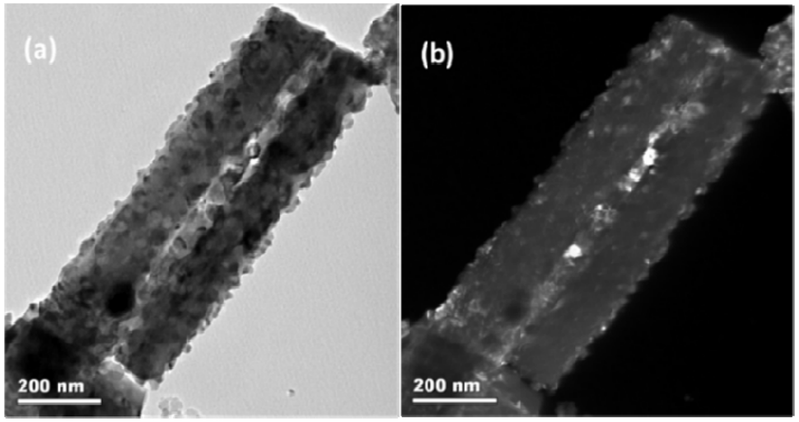


- *Solution; Zinc Acetate and Hexamethylenetetramine dissolved in Deionized Water*

Sensing material deposition (Hydrothermal method)

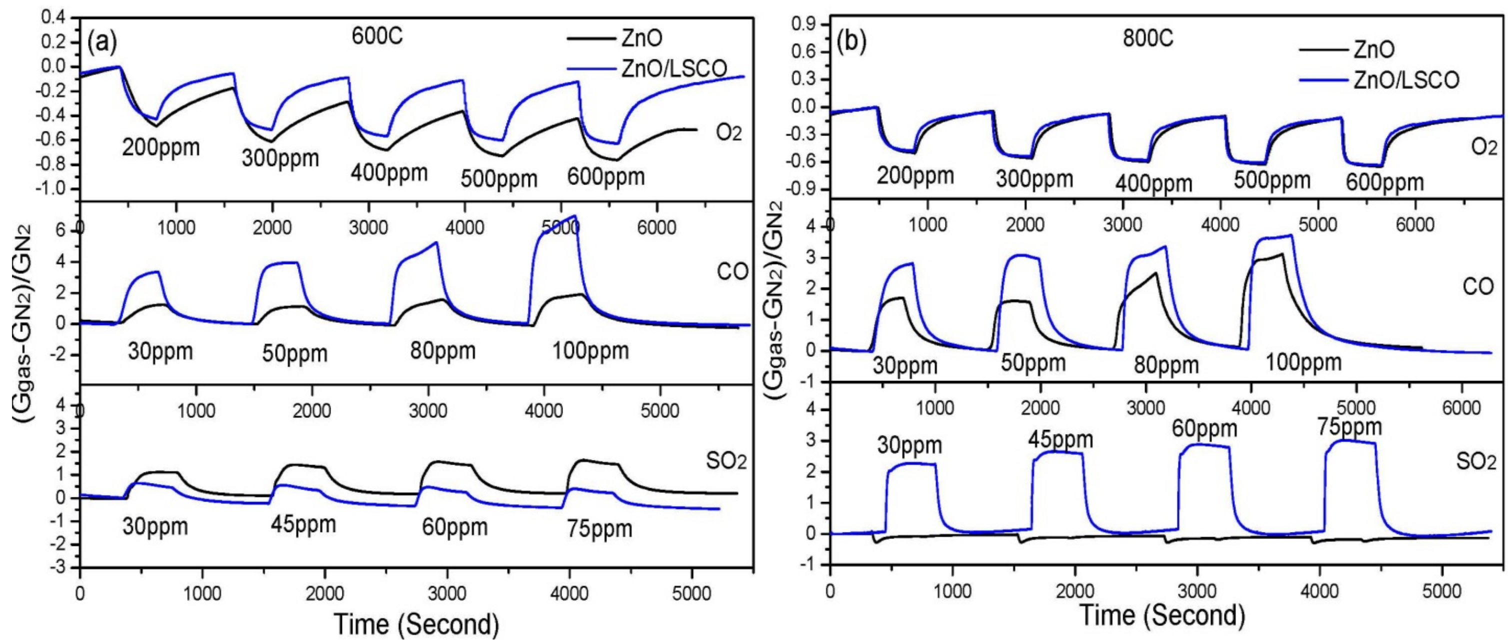


SEM images of (a) the top view of ZnO nanorod array, and (b) the side view of ZnO nanorod array



TEM images of (a) and (b) ZnO/$LaCoO_3$ core-shell nanorods

Sensing material deposition (Hydrothermal method)



The sensor performance of ZnO nanorod arrays and ZnO/LSCO composite nanorod arrays under different gas atmospheres with different concentrations at 600 °C and 800 °C.

Accomplishments & Summaries

- A complete lift-off process has been conducted and shown success in device fabrication.
- Parameters for photolithography process (lift-off) have been optimized for different kinds of substrates (Si, SiO_2 and Quartz).
- The issue in fabrication of quartz has been addressed by applying an adhesion promoter (HMDS).
- The hydrothermal method was introduced to produce 3D metal oxide nanorods.
- The promising 3D metal oxide nanorod structure has been obtained from the hydrothermal growth.

Future work

- Since the parameters of lift-off process have been optimized for a piezoelectric material (quartz), they will be applied to Langasite (LGS) as a high temperature substrate.
- Perform the wireless detection using 3D nanorod composite SAW sensor arrays with the wireless signal showing concentration-dependent behavior.
- 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
- Technician: Amehayesus Gebreyohannes in the Center for Nanoscale Systems at Harvard University
- Thank the supporting from Department of Energy and National Energy Technology Laboratory

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Center for Nanoscale Systems
Harvard University

Thank You

Questions?