Passive Wireless Sensors Fabricated by Direct-Writing for Temperature and Health Monitoring of Energy Systems in Harsh-Environments

Graduate and Undergraduate Researcher Team:
Kavin Sivaneri Varadharajan Idhaiam[a]
Harish Palakurthi[b]
Peter Dreher[b]

Co-PI Team:
Dr. Edward M. Sabolsky[a]
Dr. Kostas Sierros[a]
Dr. Daryl Reynolds[b]

[a]Department of Mechanical and Aerospace Engineering
[b]Lane Department of Computer Science and Electrical Engineering
West Virginia University (WVU)

Background- Harsh Environment Sensing Needs

In-situ monitoring of high temperature systems in extreme conditions encountered in: Chemical Synthesis; Ceramic Processing; Metallurgy/Manufacturing Industries, etc.

Harsh Environments

- High temperature (>500^{o}C).
- High pressure (up to 1000 psi).
- Various pO_2 levels.
- Corrosive conditions (molten inorganics or reactive gasses).

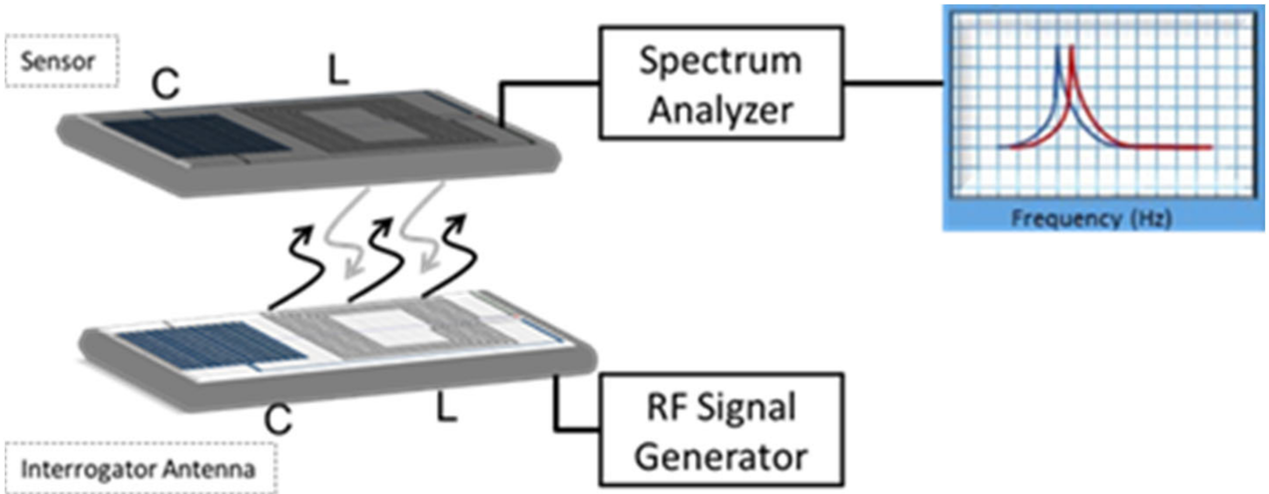
Ability to monitor:

- ✓ Temperature.
- ✓ Stress/strain components.
- ✓ *In situ* failure analysis.

Current Issues

1) Stability (Material property), 2) Sensor integration with the sensing system (Interface), 3) Reading sensor response (interconnection)

Sensing Mechanism (LC-based RF Resonator)



Sensor Components:

Planar **L (inductor)** and **C (capacitor)** deposited on a dielectric substrate.

Working Mechanism:

$\boldsymbol{\Delta T \ \alpha \ \Delta f_r}$

$$f_r = \frac{1}{2\pi\sqrt{LC}} \Rightarrow C = \frac{\varepsilon_0 \varepsilon_r A}{d}$$

ε_0 – Constant

A; d – Predefined variables

ε_r – Relative Permittivity

(ε_r α T)

Processing Vision – Peel and Stick Sensor

Item A represents the organic carrier film.

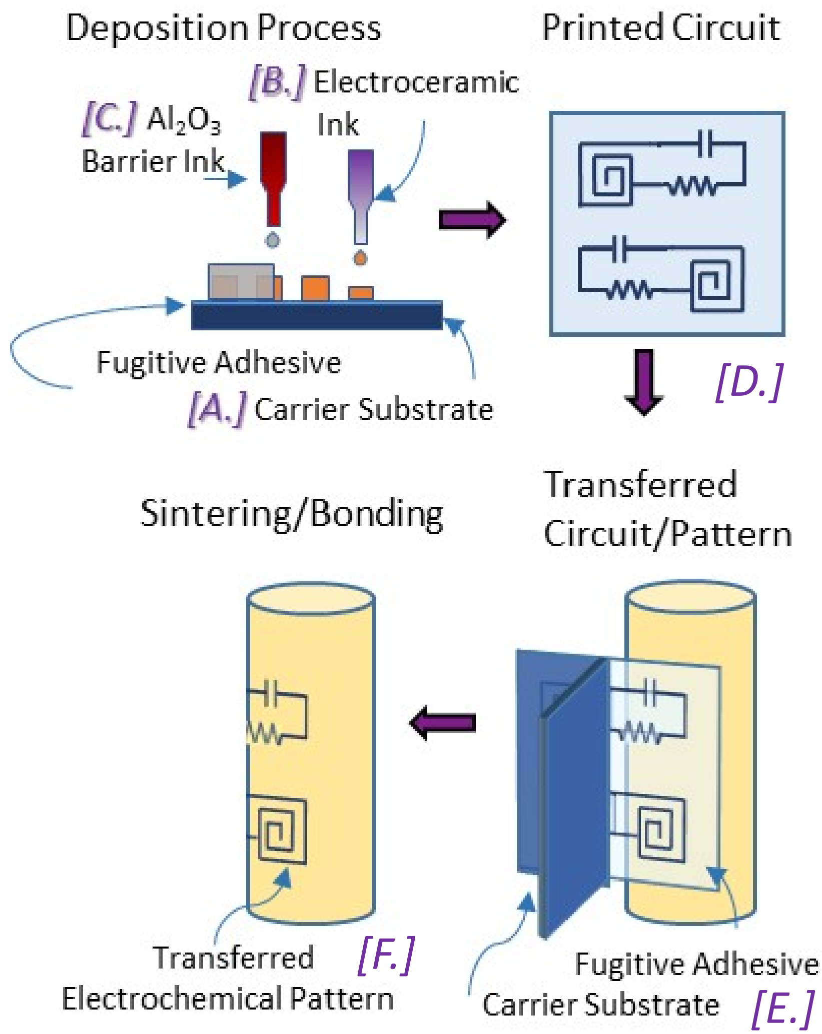
Item B represents the polymer-precursor ink (converts to an electroceramic after heat treatment).

Item C represents a possible barrier layer.

Item D represents RF circuit sensor circuit printed on the transfer paper.

Item E shows the RF circuit pattern being placed upon the energy-system component.

Item F represents the pyrolysis of the organic carrier and bonding.



Program Objectives

Task 2:

- Investigate phase formation, sintering/grain growth, and electrical properties of polymer-derived electroceramic composites between 500-1700 °C.

Task 3:

- Define processes to fabricate sensor through direct-writing (or micro-casting) electroceramic composites.
- Develop methods to form monolithic "peel-and-stick" technology.

Task 4:

- Design of RF passive wireless LCR circuits and receiver (reader) antennas for testing at temperature up to 1700°C.

Task 5:

- Demonstrate the passive wireless sensor system.

Task 2.0: Fabrication and Characterization of Polymer-Derived Electroceramic Composites. (Sabolsky, Varadharajan)

Task 2.0 Objective:

Investigate phase formation, sintering/grain growth, and electrical properties of electroceramic composites for applications at 500-1500 °C.

- **System 1:** Indium tin oxide (ITO)
- **System 2:** Lanthanum strontium chromate (LSC)

Task 2.0 Approach:

- **Subtask 2.1 Analysis of Multifunctional Electroceramic Composites:**

Electrically conducting/semi-conducting oxides namely, indium tin oxide (ITO), and lanthanum strontium chromate (LSC) will be investigated as precursors to fabricate various electroceramic compositions. This will include the addition of fillers to understand the stability.

- **Subtask 2.2 Thermal Processing of Composite Compositions:**

Samples will be pressed into bars, and also screen-printed onto Al_2O_3 or ZrO_2 dense substrates (for initial observation on shrinkage effects). Thermal processing the materials in various atmospheres (air, inert, reducing atmosphere) will be completed up to 1700^{o}C.

- **Subtask 2.3 Composite Material Testing and Characterization**

Electrical testing (at high-temperature) and phase/chemistry characterization will be completed on the polymer-derived electroceramic composites.

Task 2.0 Current status:

- **Subtask 2.1 Synthesis of Multifunctional Electroceramic Composites:**
  - ✓ ***System 1:*** Indium tin oxide (ITO).
  - ✓ ***System 2:*** Lanthanum strontium chromate (LSC).

- **Subtask 2.2 Thermal Processing of Composite Compositions:**
  - ✓ Investigated the thermal processing of the oxide systems on Al_2O_3 substrates.

- **Subtask 2.3 Composite Material Testing and Characterization:**
  - ✓ Phase/chemistry characterization is completed on the polymer-derived and oxide electroceramic composites.

Electroceramic Material Systems for LC Resonator

Material systems were evaluated based on:

- Operating temperature (500 – 1000°C; 1000 – 1700°C)
- Electrical Conductivity (high conductivity; positive temperature coefficient)
- Thermal Stability (No/minimal change in microstructure)
- Compatibility with the substrate (no interfacial reaction)

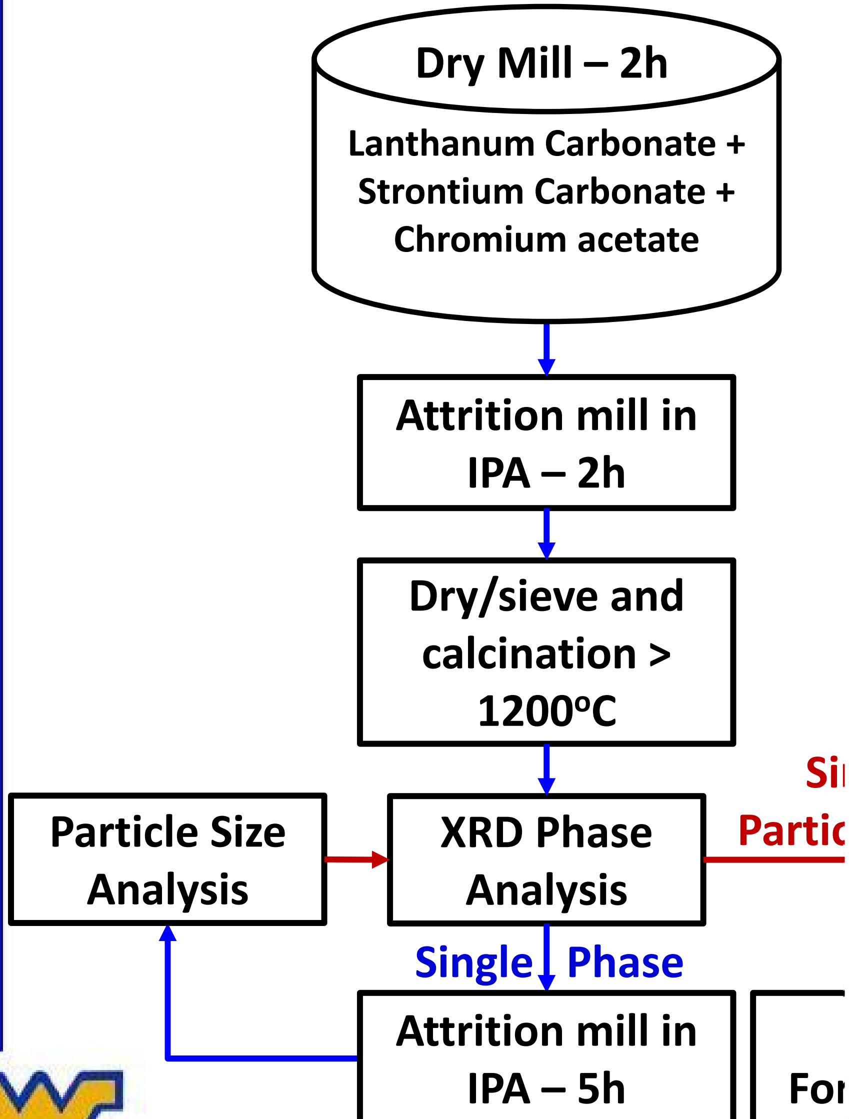
Indium Tin Oxide (ITO):

- Stable up to 1300°C.
- Electrical conductivity:>60 $S \cdot cm^{-1}$.
- Thermal stability was studies in this work.
- Good adhesion on to the substrate without the formation of secondary phase.

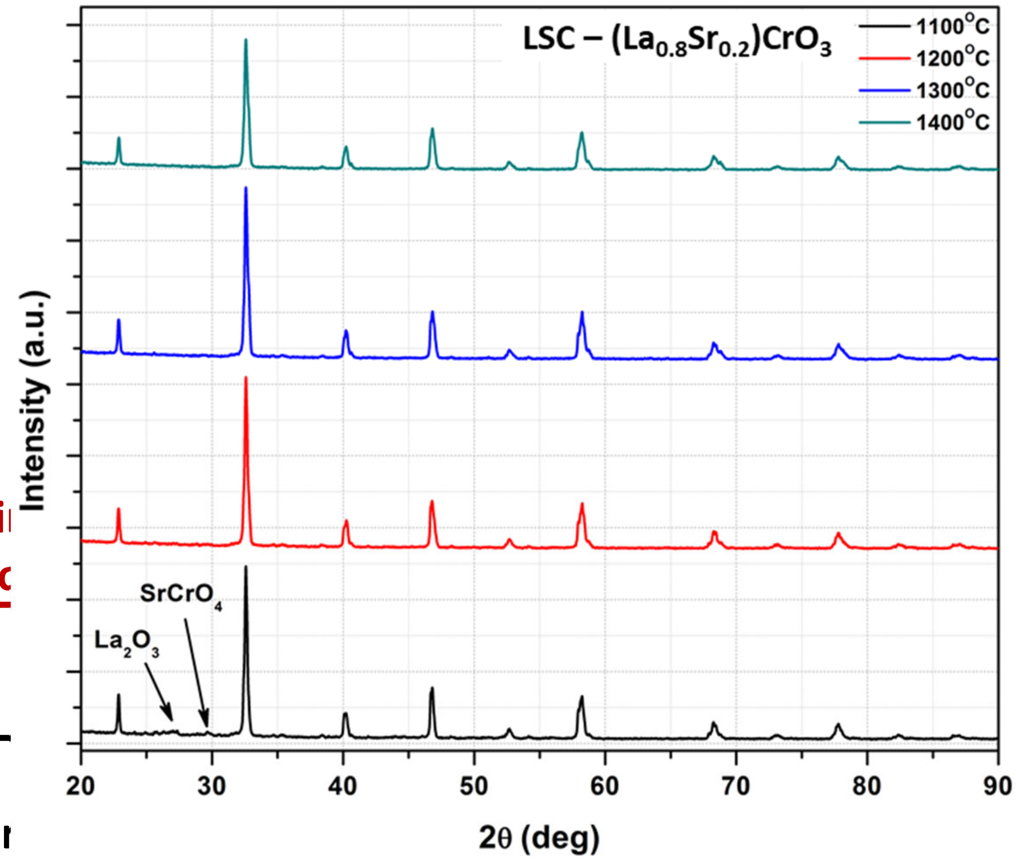
Strontium-doped Lanthanum Chromite (LSC):

- Stable up to 1800°C.
- Electrical conductivity:>3 $S \cdot cm^{-1}$.
- Thermal stability was studies in this work.
- Phase formation and compatibility with alumina substrate studied in this work.

Electroceramic Material Synthesis & Processing - LSC

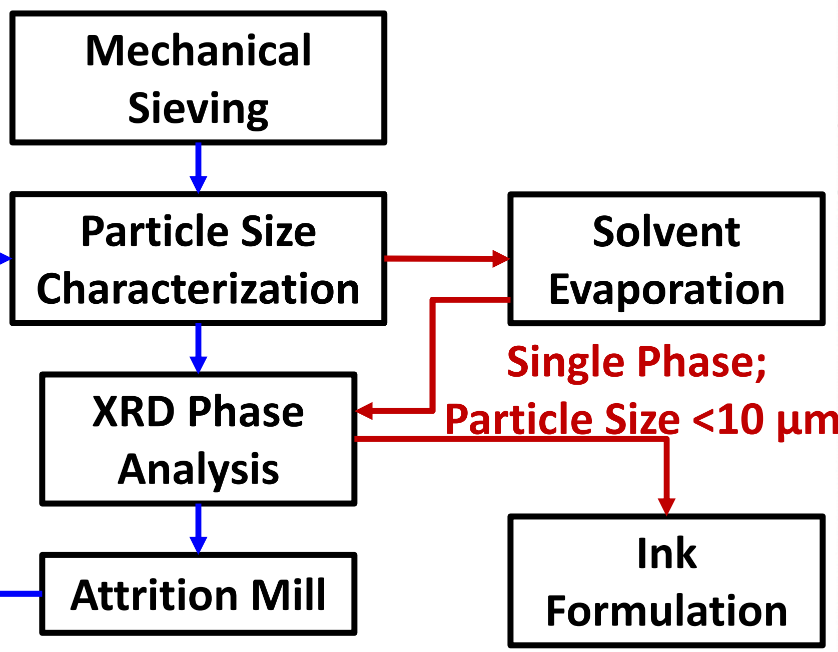


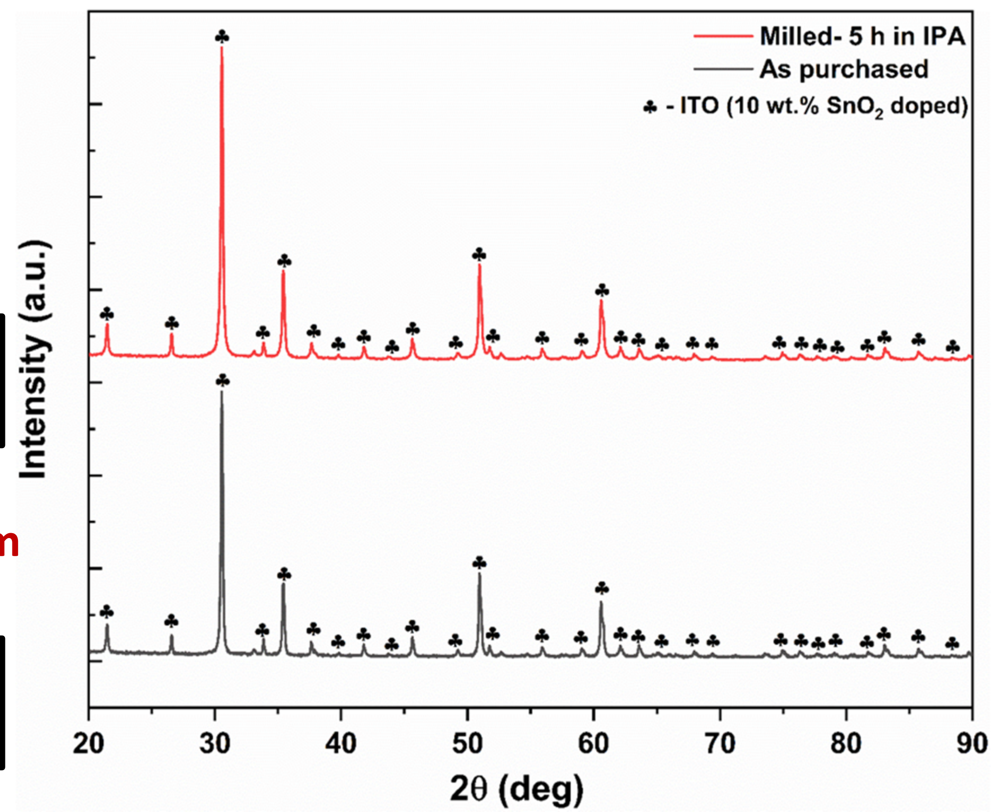
- **Solid solution** of LSC with **20% Sr** was synthesized by a **solid-state reaction** process.
- Expected phase: **$(La_{0.8}Sr_{0.2})CrO_3$**



Electroceramic Material Synthesis & Processing - ITO

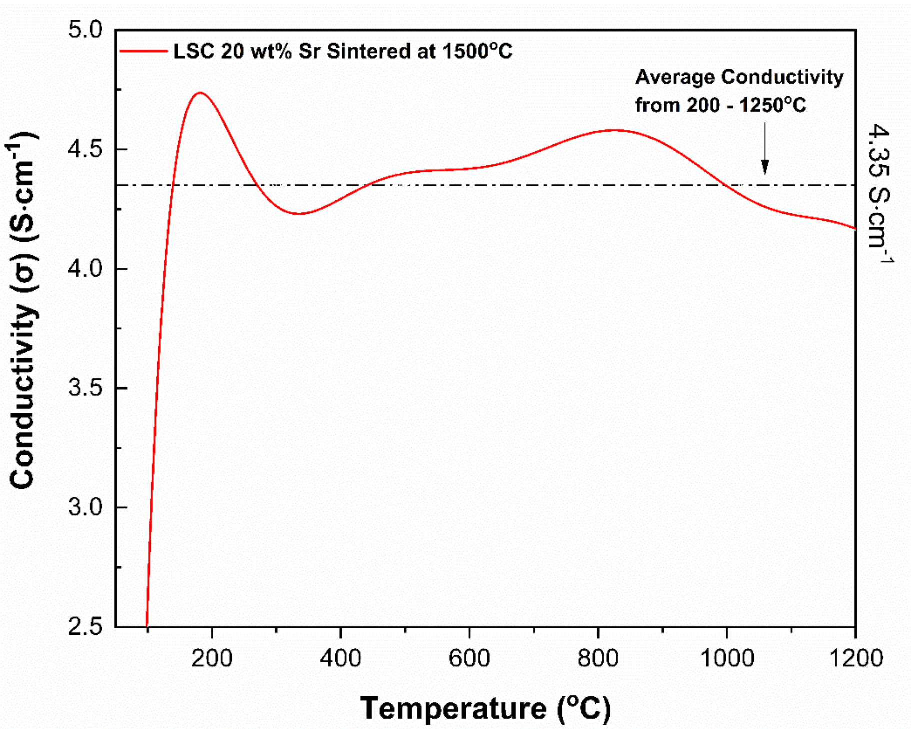
ITO (10% SnO_2 doping) was purchased from Beantown chemicals, Inc.
Processed before the formulation of functional ceramic ink for the sensor fabrication.

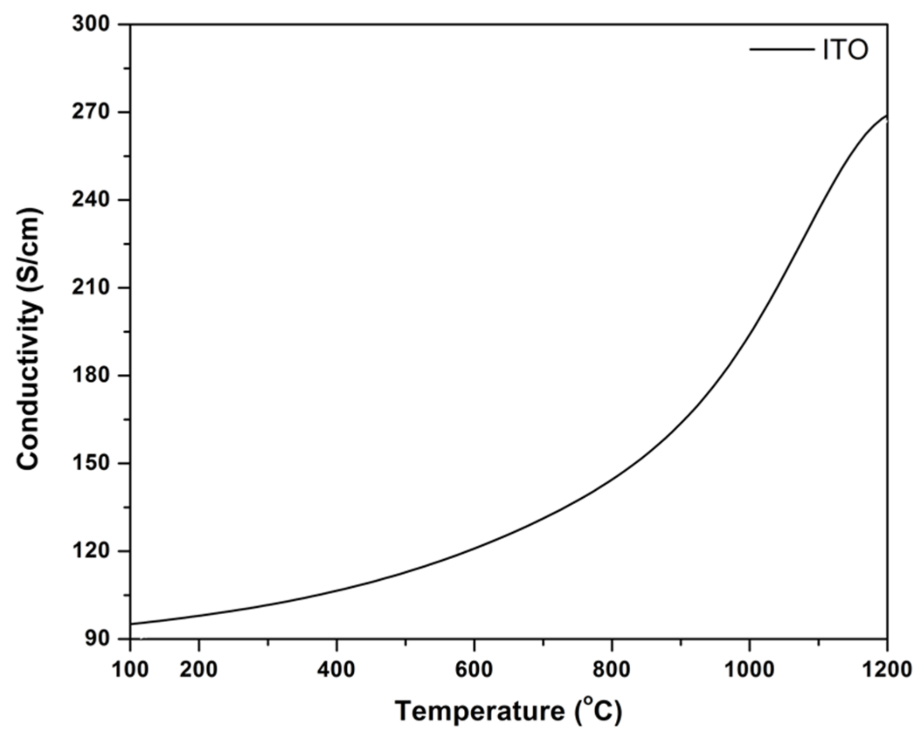




Electrical Conductivity Analysis

- Thick film conductivity (σ) with thickness ~20 μm was tested from 100 – 1250°C for both LSC and ITO.
- $\sigma_{(LSC)}$ = ~4.34 S·cm^{-1} from 200 – 1250°C.
- $\sigma_{(ITO)}$ = ~100 - 280 S·cm^{-1} from 200 – 1250°C.





*D B Meadowcroft 1969, J. Phys. D: Appl. Phys. **2 1225**

Task 2.0 Summary:

- Synthesized and characterized composites of indium tin oxide and lanthanum strontium chromate.
- The phase stability, compatibility with the substrate and electrical conductivity was analyzed.
- ITO and LSC showed good electrical conductivity for thermoelectric applications.

Task 2.0 Near-term Future Work:

- **Synthesize:**
  - Silicide-carbide systems with active and inactive (Al_2O_3, ZrO_2) fillers.
  - Characterize Durazane – 1800 (a high silicon containing polymer) by adding Mo/C to synthesize SiC or $MoSi_2$.
  - Other conductive oxide-based composites.
- Effects of thermal processing.
- Study phase formation.

Task 3.0:
Direct-Writing, Patterning, and Transfer of the Sensor System.
(Sierros/Sabolsky/Varadharajan)

Task 3.0 Objectives:

- To define processes to direct-write through ink-jet and robo-casting the polymer-derived electroceramic composites onto oxide and polymer surfaces.
- To develop a method to transfer the pattern from an organic film to a ceramic surface and bond after thermal treatment.
- To develop a process based on photolithography to fabricate smaller sensor architectures to overcome the geometrical limitation of the direct-writing process.

Task 3.0 Approach:

Subtask 3.1 Direct-Writing Process Development:

- Develop and characterize inks within a permissible surface tension and viscosity level. Direct-writing with Nordson EFD Performus VI robo-printer.
- General process for droplet deposition, drying, and thermolysis will be defined.

Subtask 3.2 Micro-Casting Process Development:

- Develop a process to pattern micro sensor design directly on a ceramic and oxide substrate.
- Determine parameters for micro-casting including the viscosity, aspect ratio, particle size distribution and thermolysis.

Subtask 3.3 Baseline Sensor Testing and Design Optimization:

- Initial sensor configurations will be designed, with focus on temperature and strain measurements. The electrical performance testing will be completed at high-temperature (500-1700 ^{o}C).

Subtask 3.4 "Peel and Stick" Development:

- Investigate methods to transfer the sensor circuit/system to the active energy system component, which will be represented by alumina and zirconia substrates.

Task 3.0 Current Status:

Subtask 3.1 Direct-Writing Process Development:

- ✓ Developed inks within a permissible surface tension and viscosity level.
- ✓ Direct-writing with Nordson EFD Performus VI robo-printer.

Subtask 3.2 Micro-Casting Process Development:

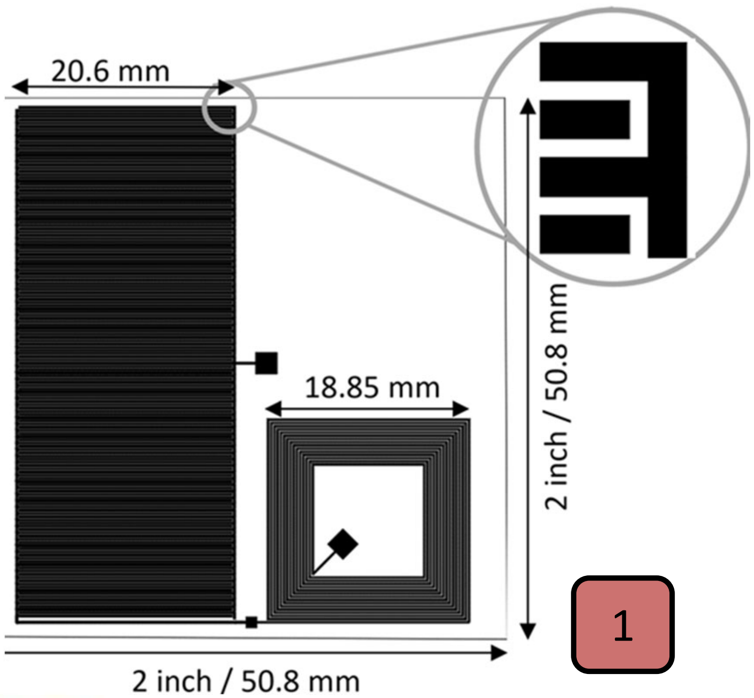
- ✓ Developed a micro-casting process based on photolithography to pattern reduced geometry sensor structures.
- ✓ Including methods to alter the wetting and drying characteristics of the deposited composite solutions.

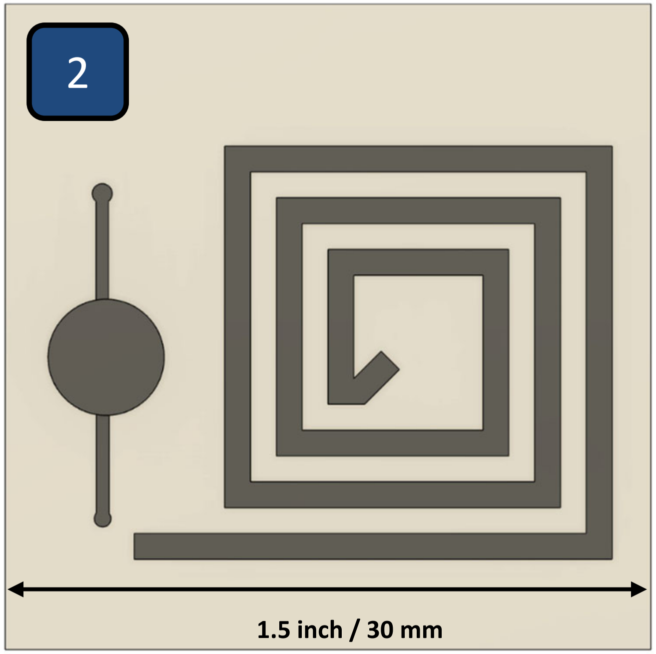
Subtask 3.3 Baseline Sensor Testing and Design Optimization:

- ✓ Ink deposited directly on oxide surfaces undergo thermal treatment defined by thermal schedules in Task 2 as a starting point.

LC Resonator Design and Simulation

- Two architectures were developed using **ANSYS/CAD** drawing software based on the working frequency range simulated by **Microwace AWR**.
- **Design 1:** 2-inch inductor/**capacitor (IDC)** pattern (fabricated by **micro-casting, direct ink writing**).
- **Design 2:** 1-inch inductor/**parallel plate capacitor** (fabricated by **screen-printing**).

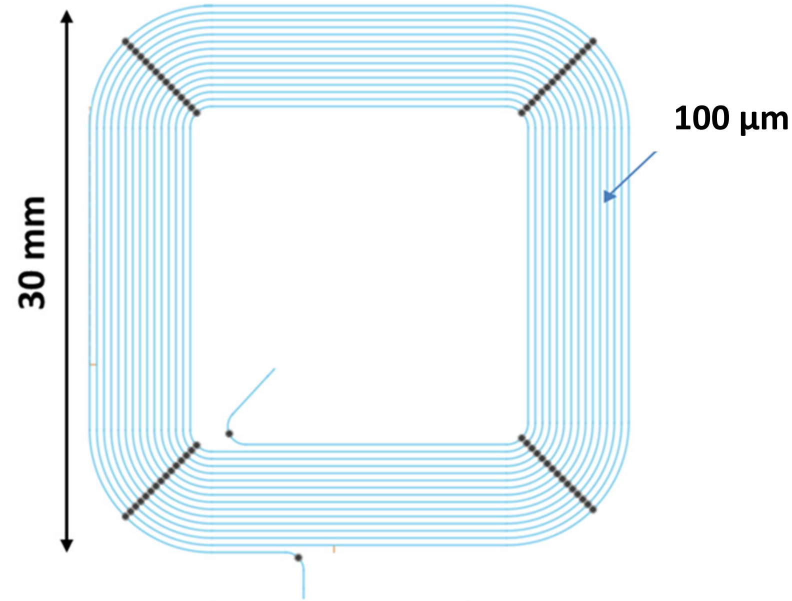




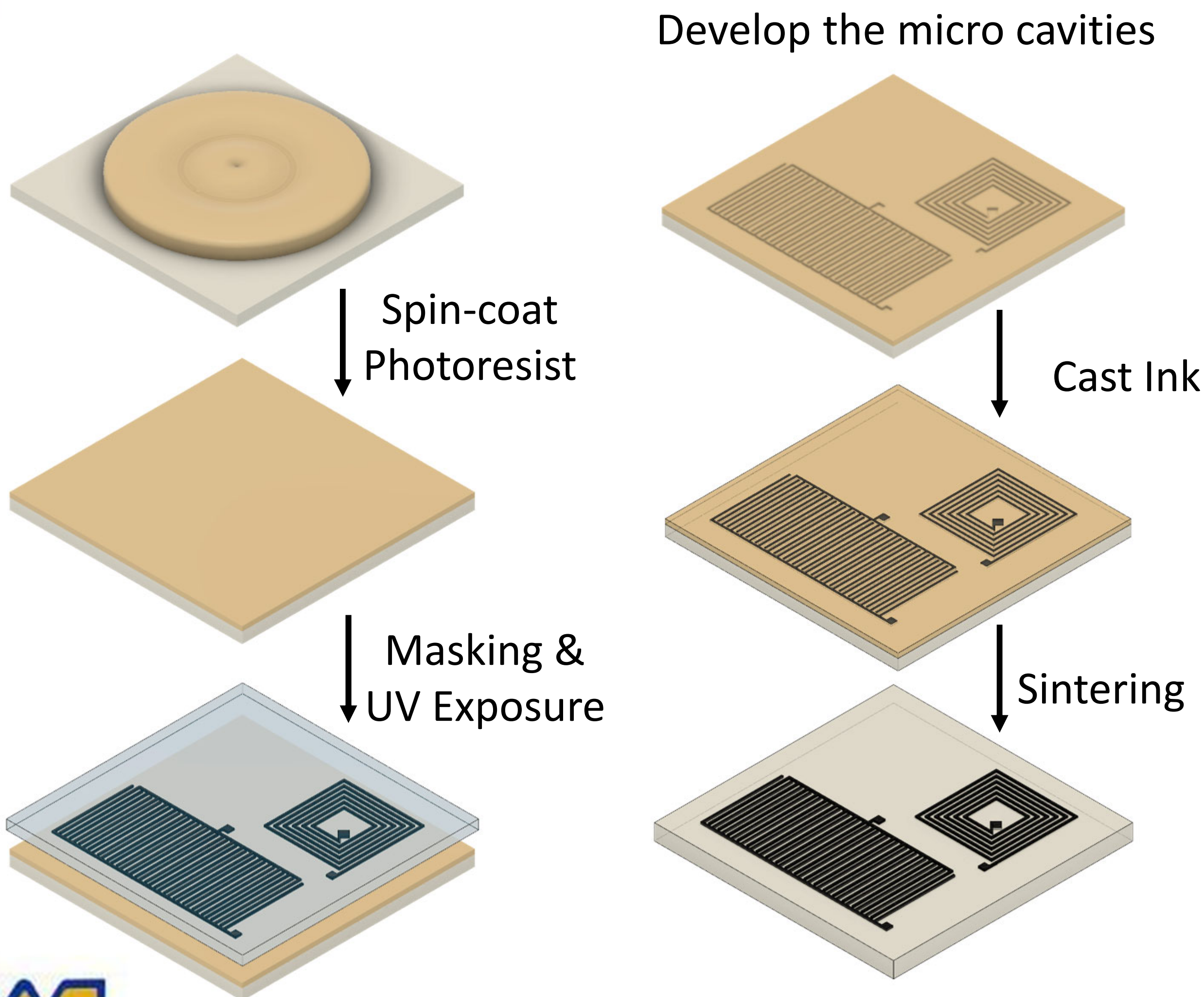
Inductor Schematic – Design 3

The inductor pattern was drawn and simulated by ANSYS/CAD software based on the working frequency range.

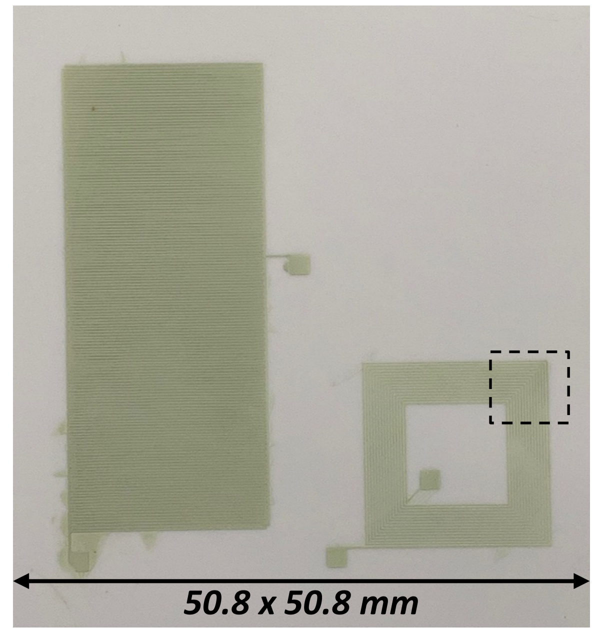
- **# of turns: 15**
- **Distance b/w the planar electrodes: 100 µm**
- **Theoretical width of the electrodes: 150 µm**
- **Overall dimension: 30 mm**

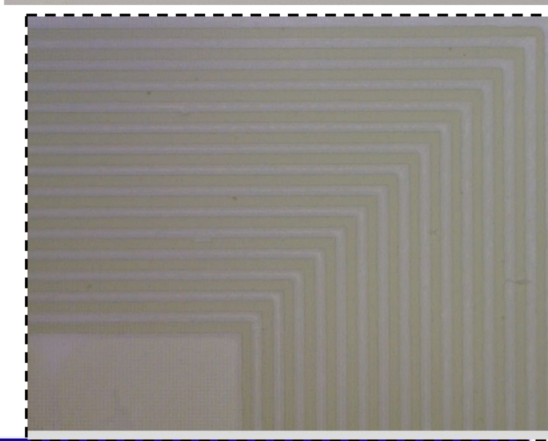


Micro-Casting Process:



50.8 x 50.8 mm sensor design on Al_2O_3 substrate.





Capacitance Analysis of the Parallel Plate Capacitor

- Top & Bottom electrode: **3 layers of ITO (~60 μm)**
- Dielectric layer: **3 layers alumina (~60 μm)**

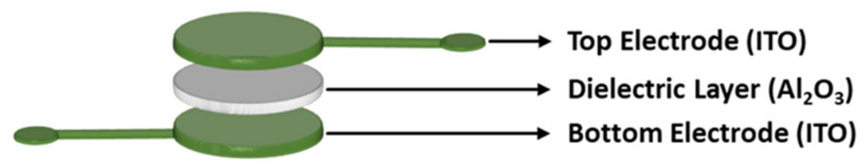
○ The **full ceramic parallel plate capacitor** was tested to **understand** the capacitive response as a function of temperature (**C vs T**).

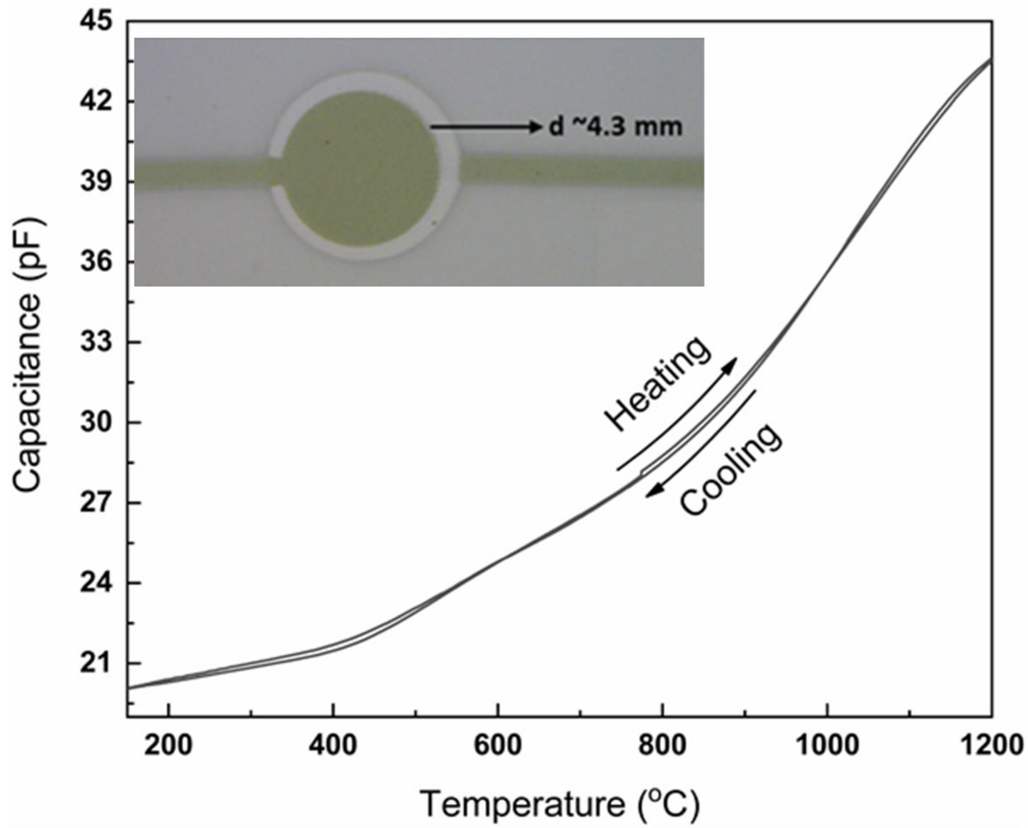
○ **ΔC = ~2 pF/100ºC.**

○ The **ΔC** remains the **same** during the **heating/cooling** cycles.

Since the C does not show hysteresis, the wireless response will not have hysteresis.

Schematic of Parallel Plate Capacitor

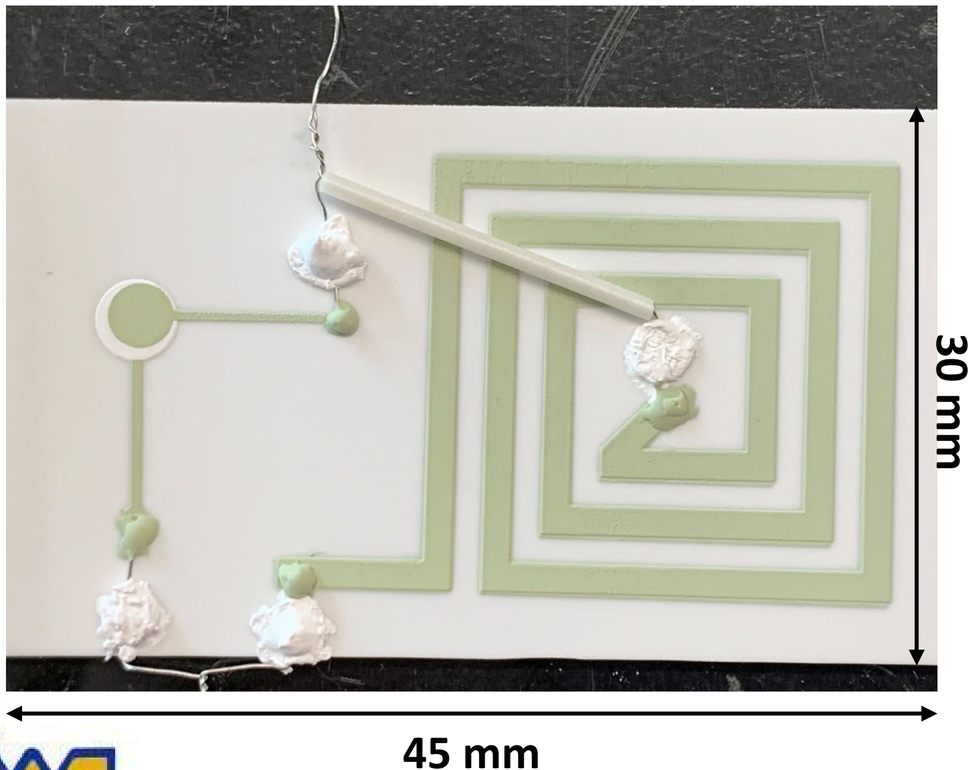




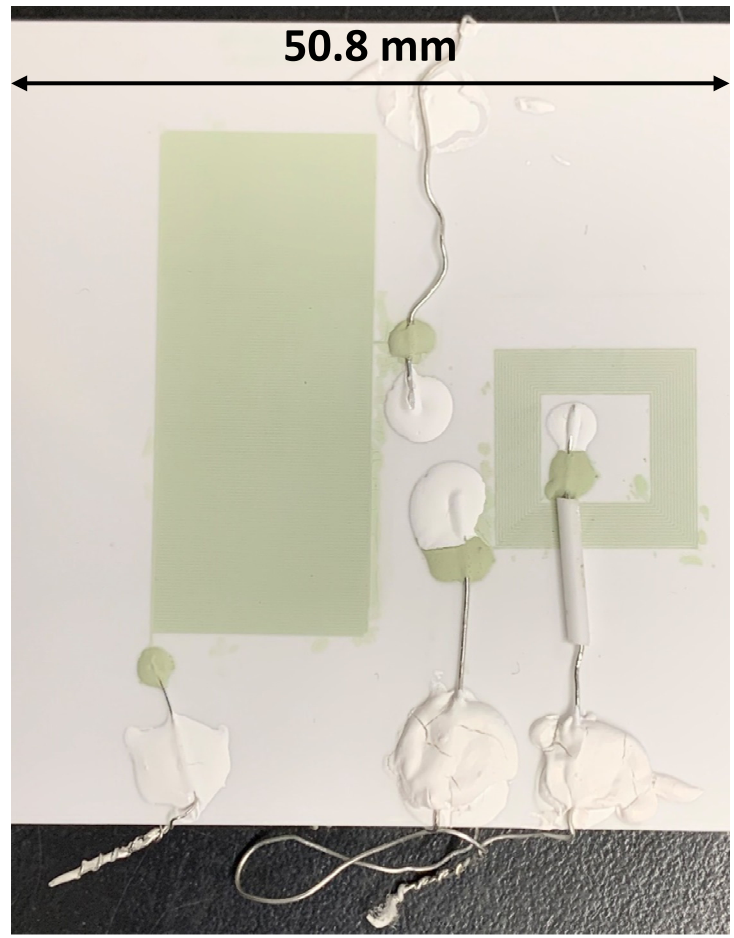
Micro-Casted and Screen-Printed LC Resonators for Wireless Chracterization:

The LC Resonators were interconnected with Pt wires to complete the LC circuit as shown in the figure.

Parallel Plate capacitor/Macro Inductor



IDC/Micro-Inductor



Direst Ink Writing – Ink Formulation

Ink Synthesis Process

1:1 EtOH-Toluene
+
Fish Oil

+ ITO Particles

↓

Roll Mill 4 h

↓

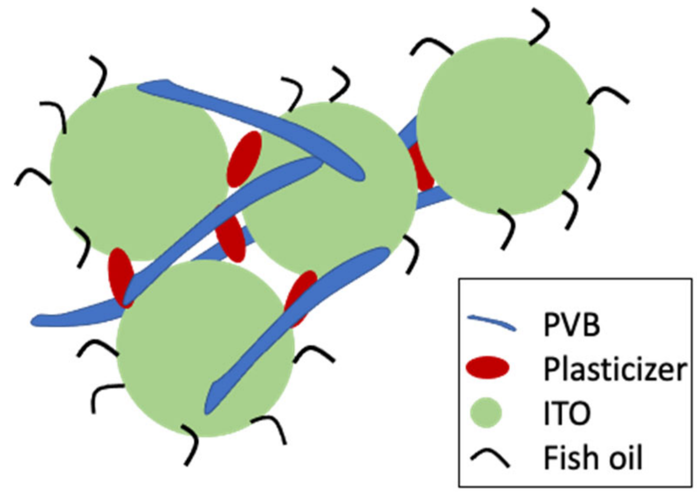
Binder (PVB) + Plasticizer (S-160)

↓

Roll Mill ~18 – 24 h

- **Dispersant: Fish oil**
- **Binder: Polyvinyl butyral (PVB)**
- **Solvent: Ethanol – Toluene**
- **Plasticizer: Butyl benzyl phthalate (S-160, tape casting warehouse, Inc.)**

Schematic of the Ink Formulation Mechanism



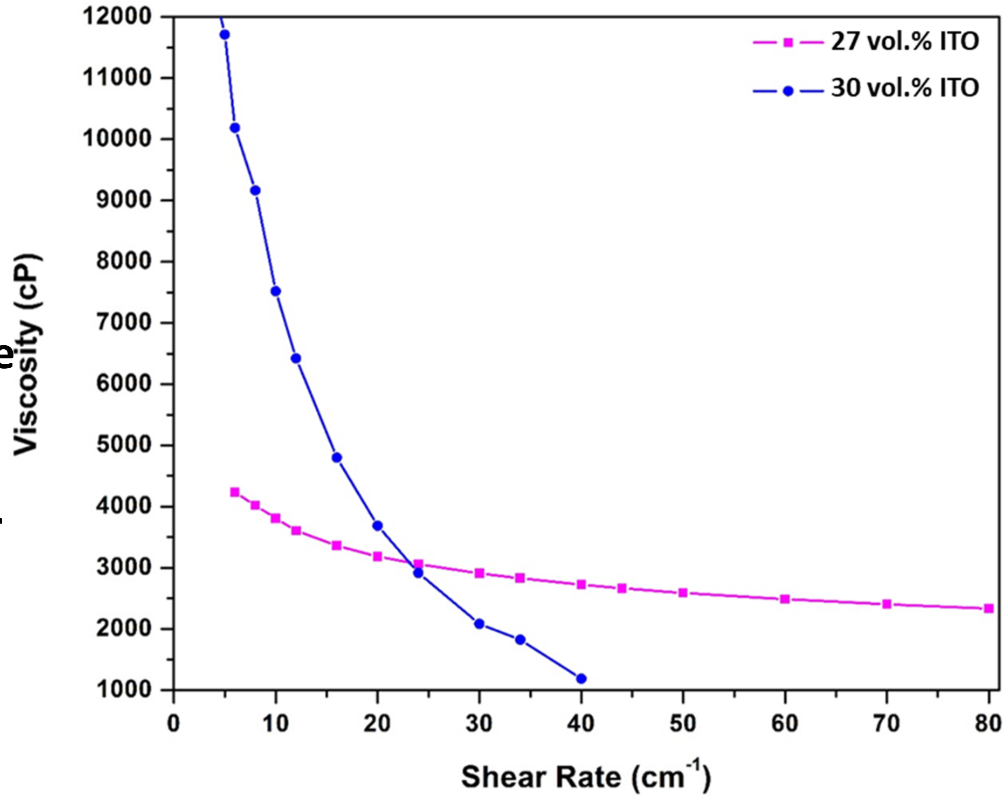
Two different wt.% of solids loading were prepared for further characterization.

Ink Characterization

- **30 vol.% starts with higher viscosity due to high solids loading.**

- **Shear thinning occurs rapidly for the 30 vol.% due to high probability of particle-particle interaction during the shearing.**

- **A semi-linear is shearing observed for 27 vol.% solids loading due to steady disentanglement of the organic materials present in the ink.**



Key Rheology Parameters:

- **Shear thinning at low shear rate.**
- **Average viscosity between 1500 – 5000 cP.**
- **Limited wetting to retain dimensions.**

Direct Ink Writing (DIW) Process

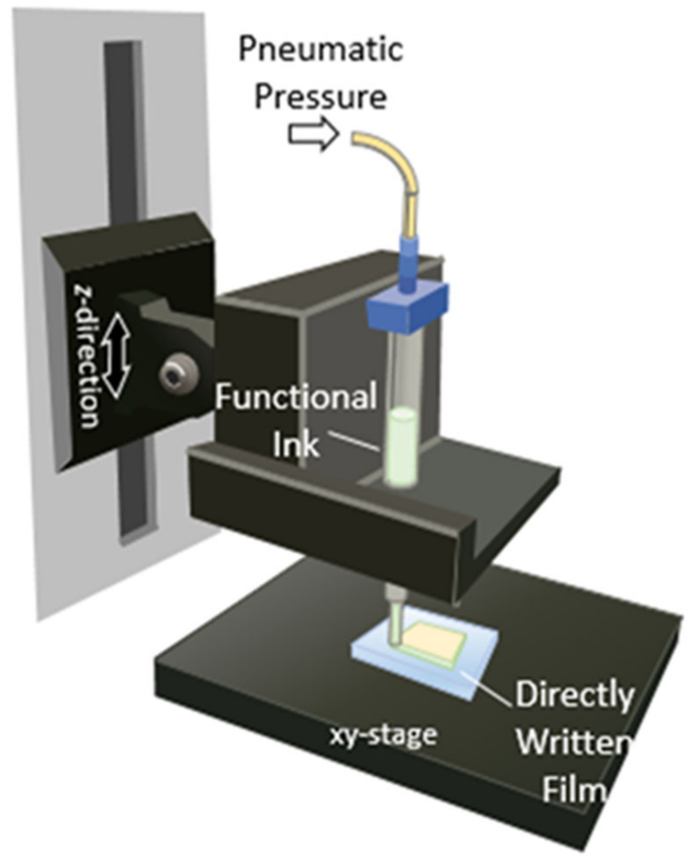
Nozzle-based robotic deposition (NBRD) system was employed.

Pneumatic pressure (causing shear thinning) controls the ink flow rate.

The xy-stage was controlled by a computer for optimizing design parameters.

- **Syringe: 5 cc**
- **Nozzle diameter: 27 (200 µm) and 30 (150 µm) gauge**
- **Print rate and pressure was manipulated to optimize the print resolution and consistency.**

DIW process schematic



DIW Process Optimization

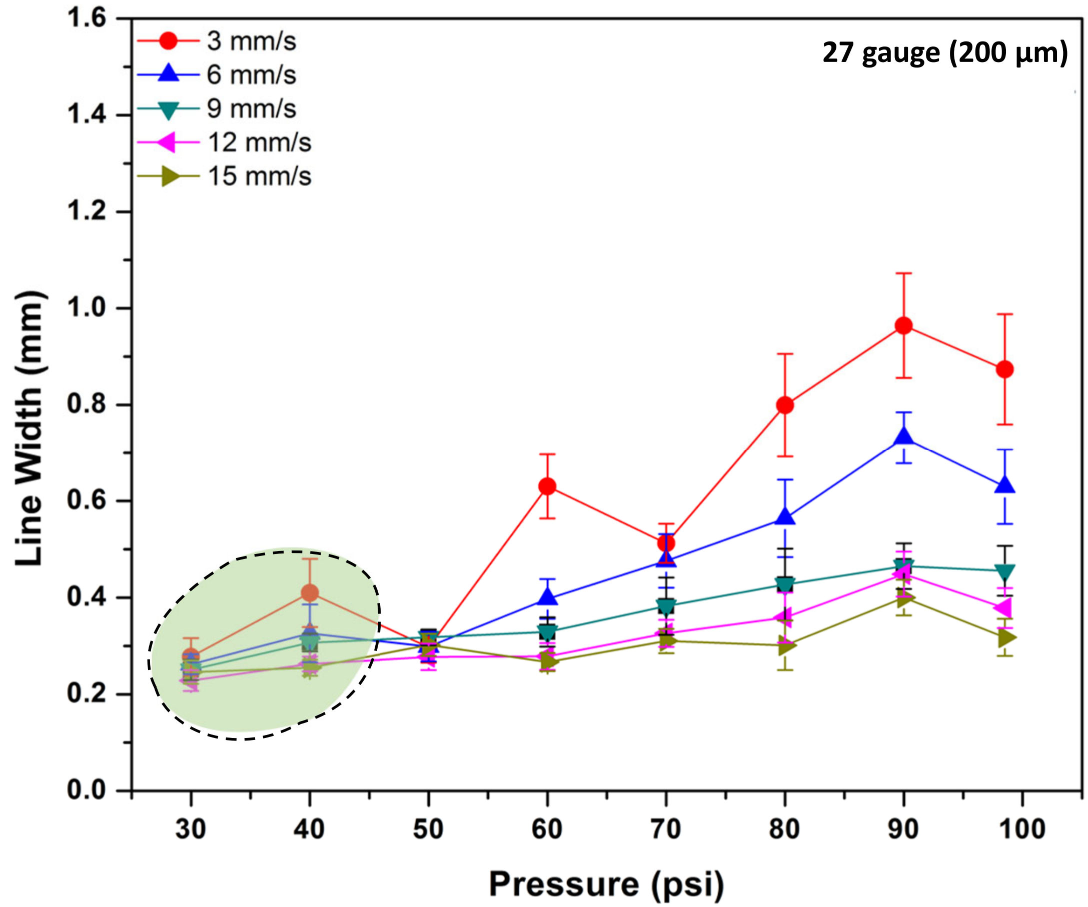
Adjacent 30 mm line was deposited on the alumina substrate with different print rates and pressure.

The ink showed good adhesion and wettability on Al_2O_3 substrates (R_a ~2- 5 µm).

- **Ink: 30 vol.% ITO**
- **Print rate: 3 – 15 mm/s**
- **Pressure: 30 – 100 psi**

- **Low pressure regime (30 – 40 psi) yields lower thickness with minimal standard deviation.**

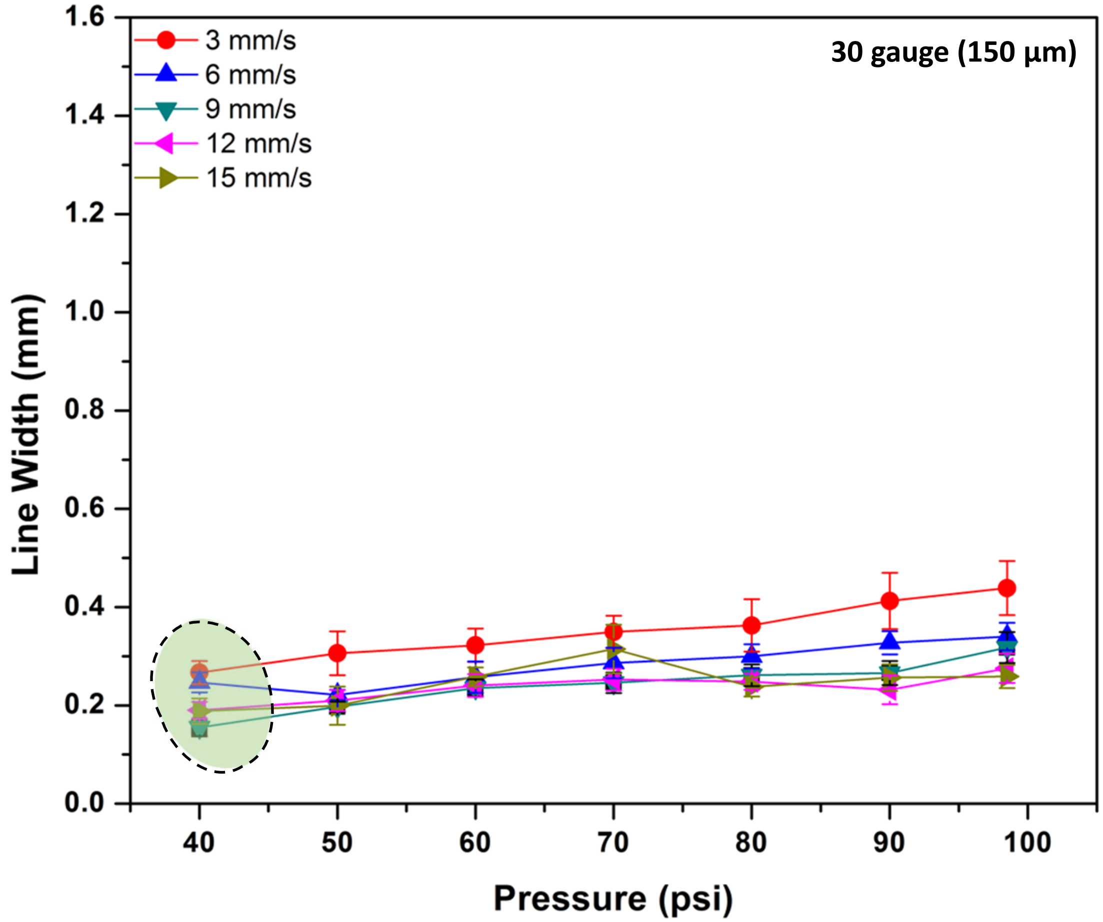
- **Increased pressure and low print causes inconsistency and higher line thickness.**



DIW Process Optimization

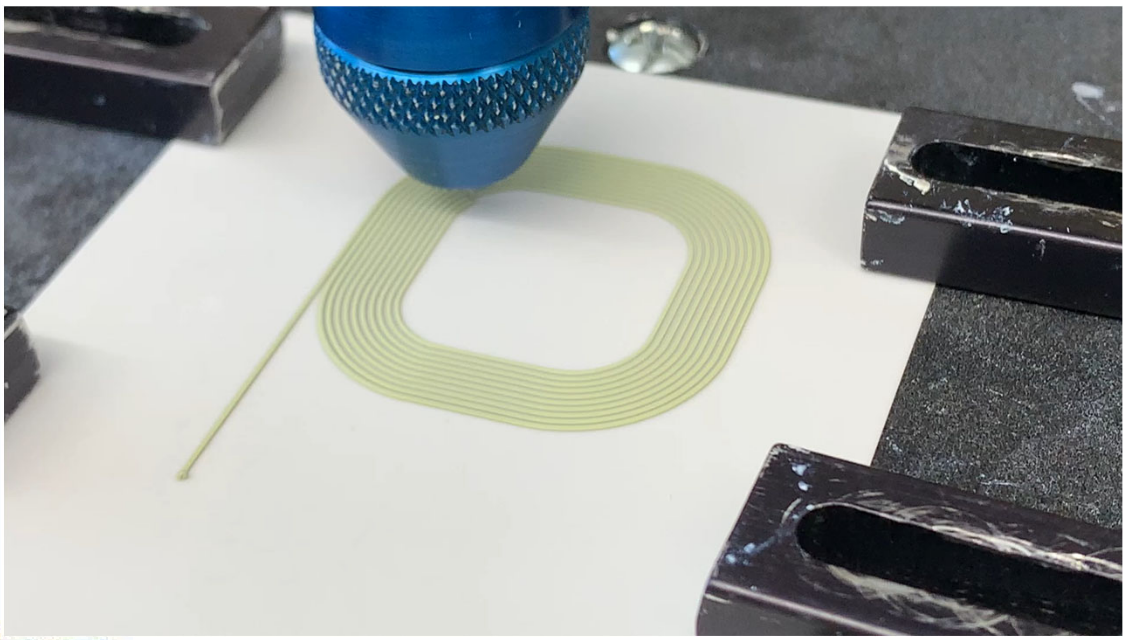
Multiple 30 mm line was deposited on the alumina substrate with different print rates and pressure.

- **Same conditions were used for 30-gauge nozzle diameter.**
- **Irrespective of the print rate there is a linear increase in line width with respect to pressure.**
- **9, 12, & 15 mm/s @ 40 psi yields the minimum line width of ~145 – 150 µm.**

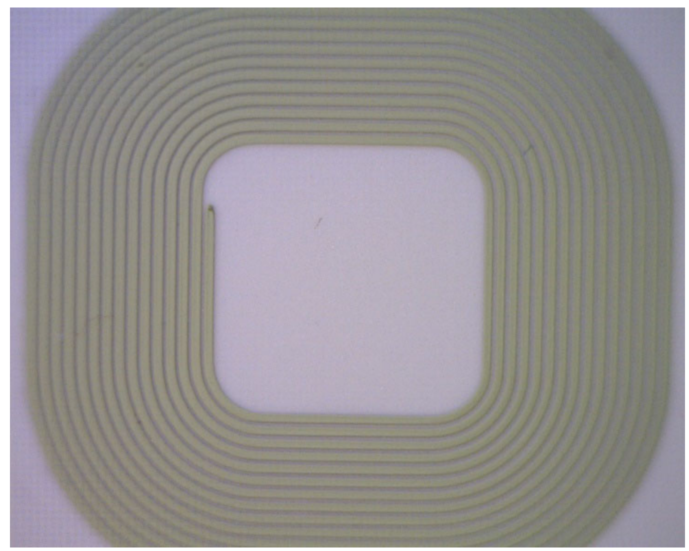


Demonstration of Direct Writing Process – ITO

- **Parameters:**
  - **Ink: 30 vol.% ITO**
  - **Nozzle: 30 gauge (150 µm).**
  - **Print speed: 9 mm/s.**
  - **Line width : ~155 µm.**
  - **Line spacing: ~100 µm.**

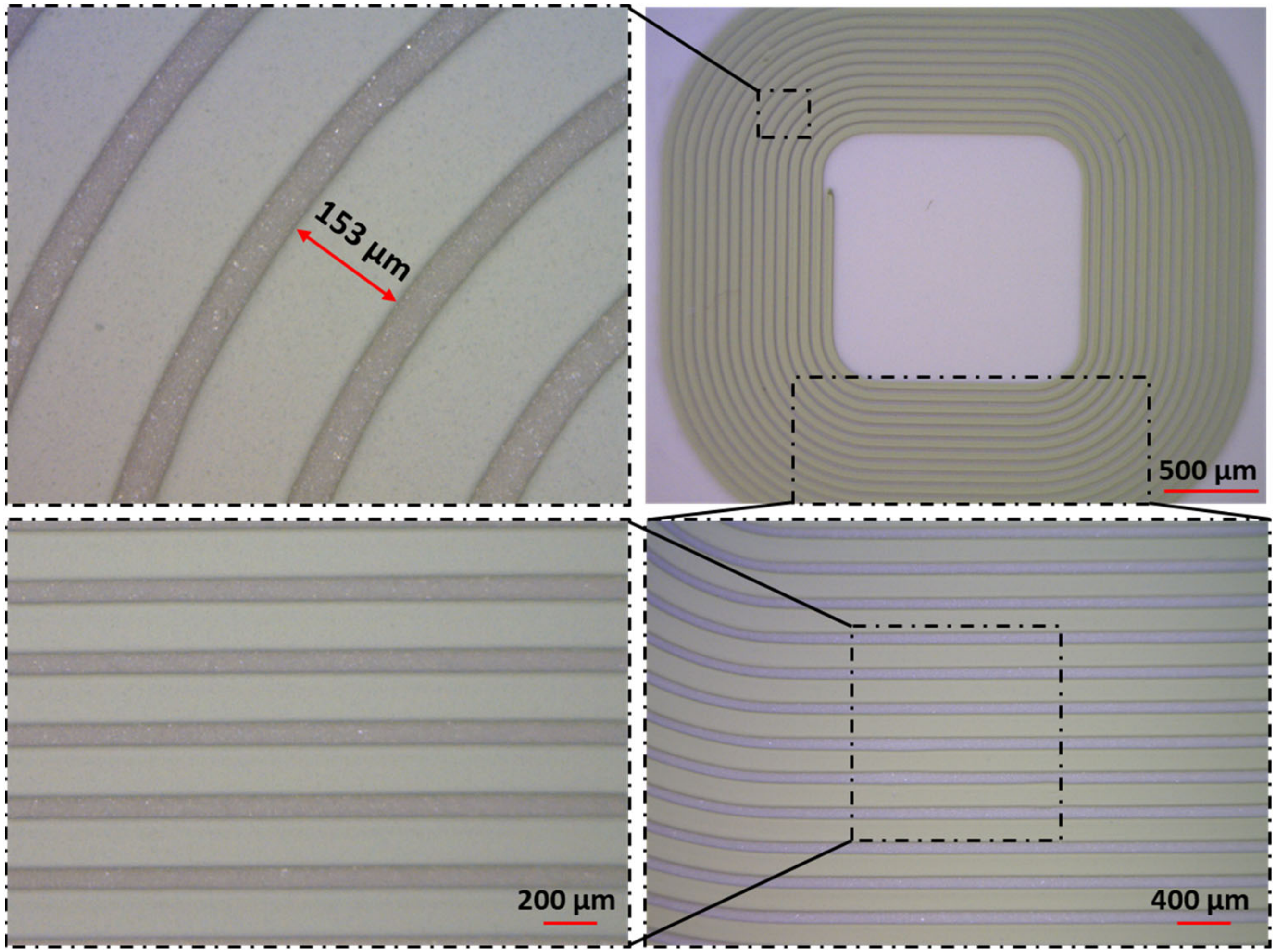


Optical Microscope Image of a Direct Written Inductor on Alumina Substrate

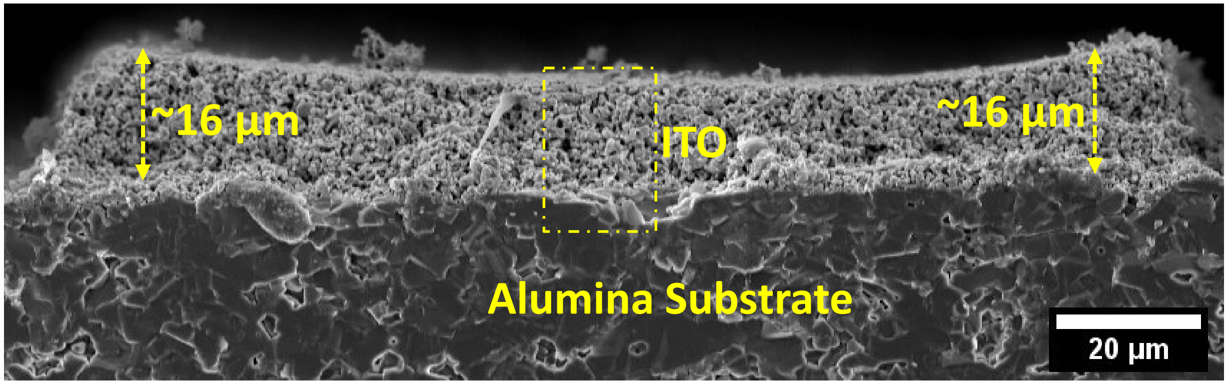


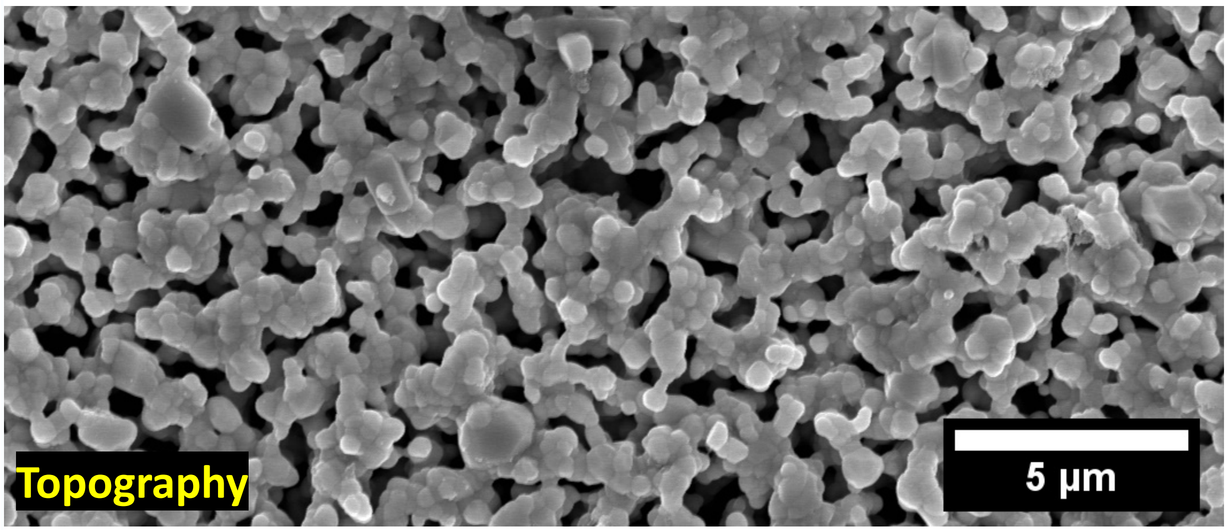
Optical Microscope Analysis of the ITO Inductor Sintered – 1250^{o}C

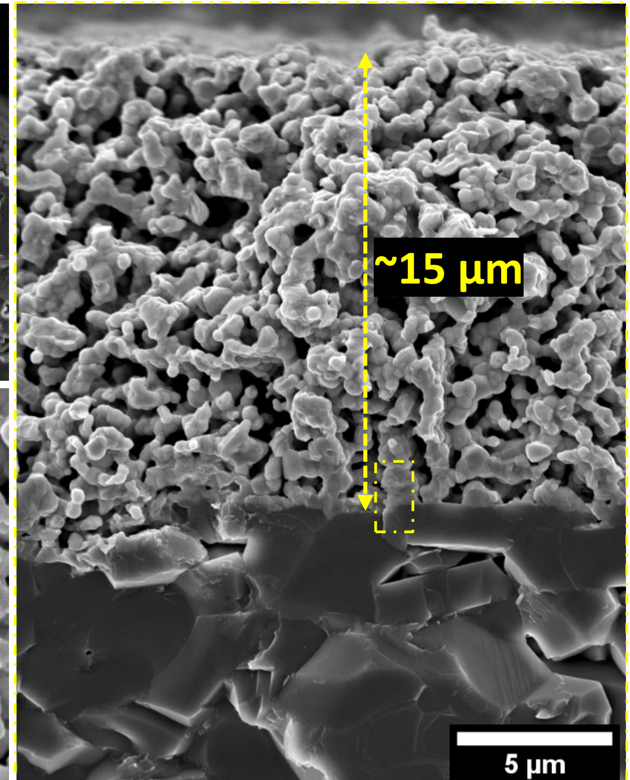
High resolution planar inductor was printed on alumina substrate with a line width deviation of ±5 µm.

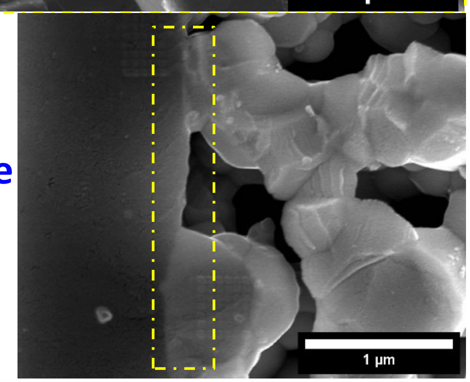


Microstructure Analysis of ITO the Inductor Sintered – 1250^{o}C









Average Grain Size: ~0.5 µm (0.2 – 1 µm).

No Interfacial diffusion can be seen at microscopic level

Task 3.0 Summary:

- Micro-casting process followed to fabricate smaller form factor sensors: 2 – inch and 1 – inch designs (parallel plate) for wireless testing and evaluation.
- Initial direct analysis of the particle dispersed in polymer ink was evaluated to fabricate ITO sensors (design 3).
- Microstructural stability of the ITO sensors were evaluated for isothermal hold up to 96 h at 1050^{o}C showing no change in the grain size.
- Screen-printing was used to fabricate the parallel plate capacitor and the sensor design-2.

Task 3.0 Near-term Future Work:

- Robo- cast preceramic ink precursors (ITO and LSC) onto oxide substrates and optimize firing temperature for optimum density.
- Achieve print resolution ~150 – 200 um to print next generation LC circuits.
- Translate the technology and print LSC on alumina substrate to carry out wireless characterization up to 1500^{o}C.

Task 4.0: Passive Wireless Communication Circuit Design and Testing. (Reynolds/Pozo)

Task 4.0 Objectives:

- Design and model passive wireless sensors and interrogator antennas as RLC circuits
- Fabricate and test the sensor up to 1200^{o}C
- To extend sensor performance up to > 1500^{o}C
- Advanced materials/writing processes => existing sensing strategies don't work!
- ***Innovation:*** *advanced materials, advanced processes,* ***robust and adaptive signal processing***

Task 4.0 Approach:

- Design RLC circuits via simulation for various material properties

- Develop a robust and adaptive signal processing approach to measure temperature wirelessly. *Ink/substrate material characteristics may not be know precisely or may change with heating/cooling cycles* ***=> tracking the resonant frequency doesn't work!***

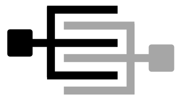
- **Modify circuits and signal processing as needed for advanced materials and high temperatures.**

Task 4.0 Current Status:

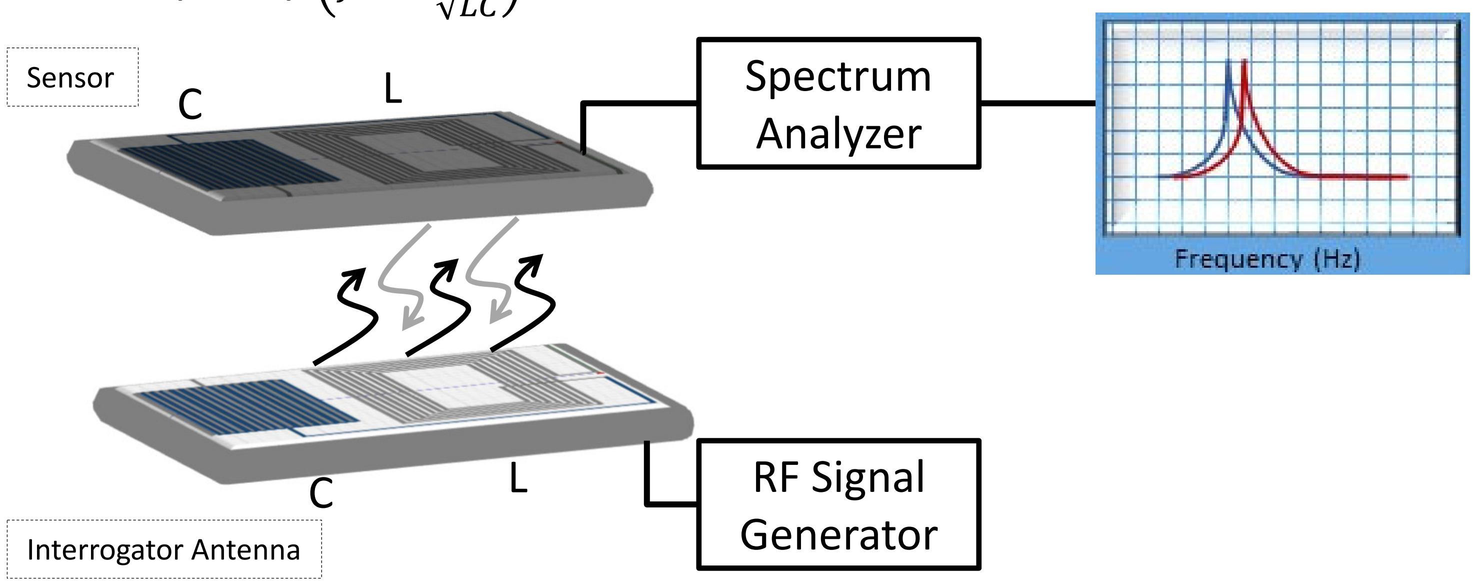
- ✓ Completed wireless characterization of LNO-Al_2O_3 (design-2) sensors from 500 – 1000°C.
- ✓ New algorithms were developed to replace conventional signal processing techniques for improves data analysis.
- ✓ Begun high-temperature characterization with pure oxide based electro-ceramic material systems: ITO and LSC.
- ✓ Reduced sensor size: 4 inch -> 2 inch -> 1 inch

Idealized LC Passive Sensing (state-of-the-art)

- An inductance coil (L) and a capacitor (C) form the LC circuit and are placed on the surface of the sensor / interrogator.

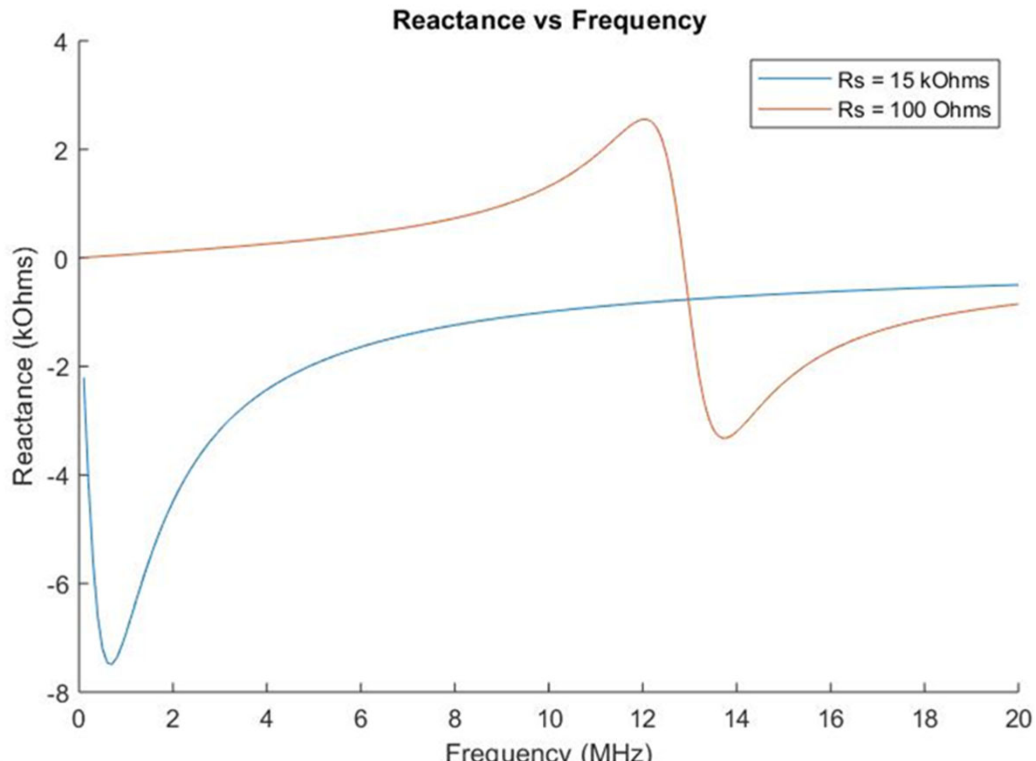
  Capacitor using microstrip lines (IDC) $\longrightarrow$ 

- Main idea: the capacitor is temperature dependent which causes shifts in the sensor's resonant frequency $\left(f \propto \frac{1}{\sqrt{LC}}\right)$



Simulation of Resistivity on Reactance vs Frequency of the Inductor

- **Reactance determines whether the component is capacitive or inductive. Inductor should have +ve reactance whereas the capacitor will show –ve reactance.**
- **High resistance of the planar inductor electrodes (15 kΩ) causes -ve reactance. (-ve reactance decreases the inductive coupling of the inductor)**
- **Lower resistance (100 Ω) shows +ve reactance at the operating frequency region.**



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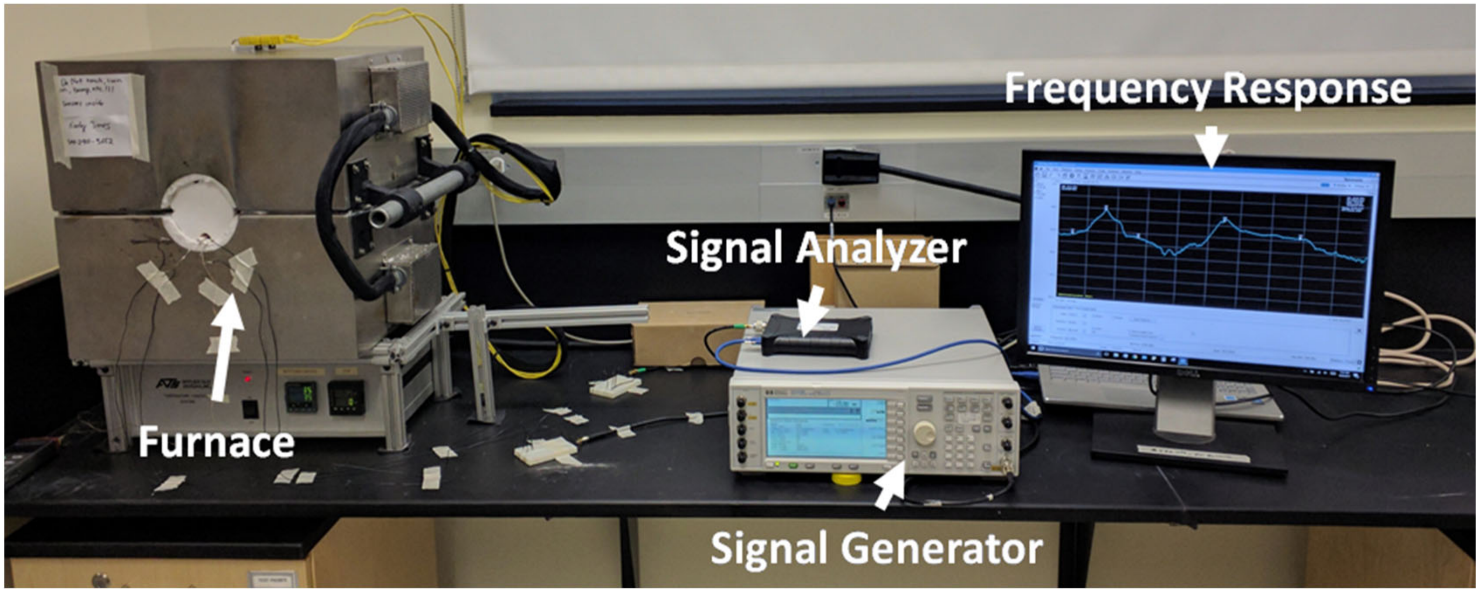
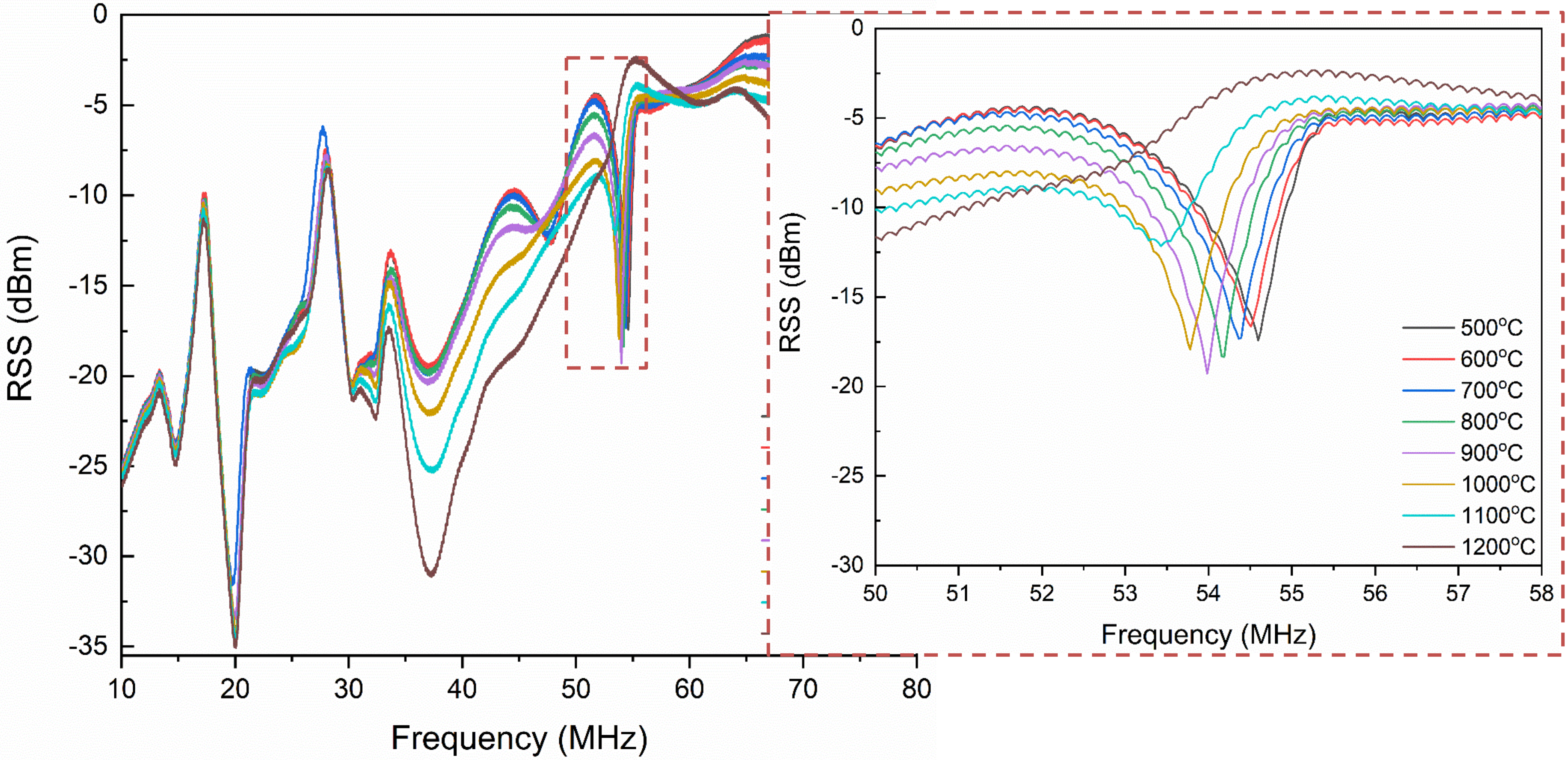
Sensor Characterization Setup



- **Two LC resonators were used to characterize the wireless signal response.**
- **One is connected to signal generator and the other to signal analyzer.**

Wireless Characterization of the Sensor Design-2: ITO Electrodes



- **Temperature signatures of the sensor from 500 – 1200°C.**
- **The peak shift can be distinguishably observed for each temperature.**
- **Temperature signatures are unique and distinguishable with a sensitivity of 3 kHz/°C.**

Frequency Analysis & Signal Processing Mechanism

- Data was analyzed by performing modular and piecewise comparison of frequency instead of entire spectrum.

2 algorithms were used to analyze the data:

  - Minimum absolute Error finds the minimum difference absolute error between unknown reading data and the signatures.
  - Cross-Correlation finds the degree of similarity between unknown reading and signatures.

Sliding Window (12 matching):

- Sliding-window of frequency size: 5, 10, 50, 100, 500, 1000, 2000, 2400.
- Example of a sliding window with a window size of 5.

✔ - Match

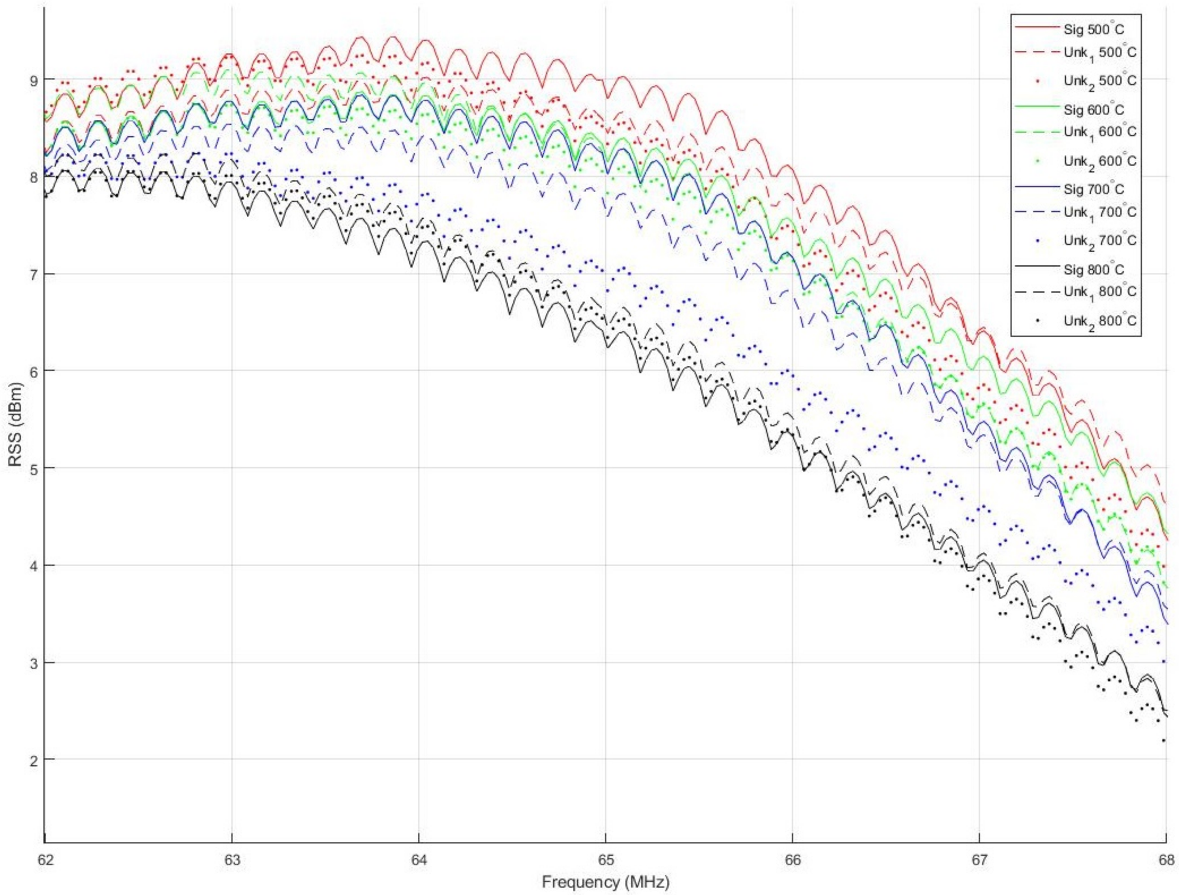
✗ - Not a match

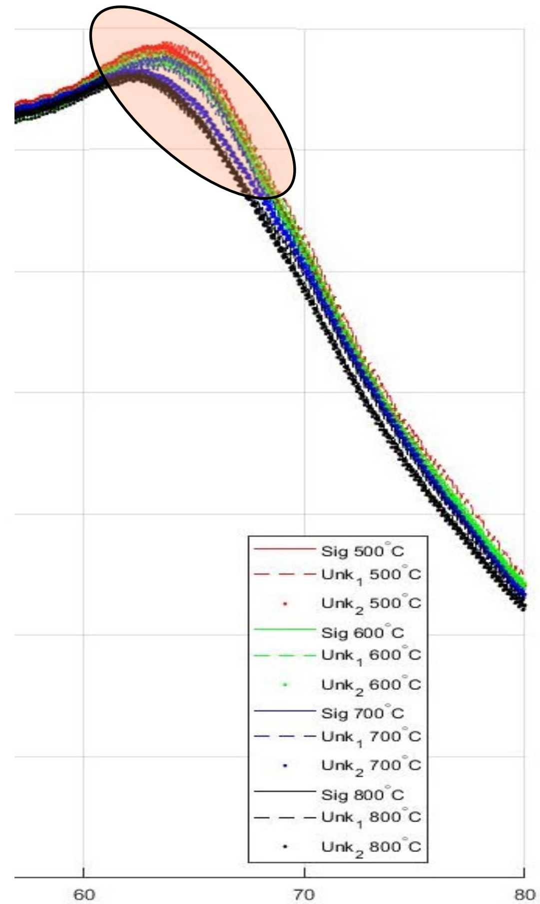
Signature	10.0000	10.0292	10.0583	10.0875	10.1167	10.1458	10.1750	10.2042	10.2333	10.2625
Unknown	10.0000	10.0292	10.0583	10.0875	10.1167	10.1458	10.1750	10.2042	10.2333	10.2625

- Optimal window size – 500 : 50 to 58 MHz

500°C- ✔ ✔; 600°C - ✔ ✔; 700°C- ✔ ✔; 800°C- ✔ ✔; 900°C- ✔ ✔; 1000°C- ✔ ✔

Wireless Characterization of the Sensor Design-1: ITO Electrodes



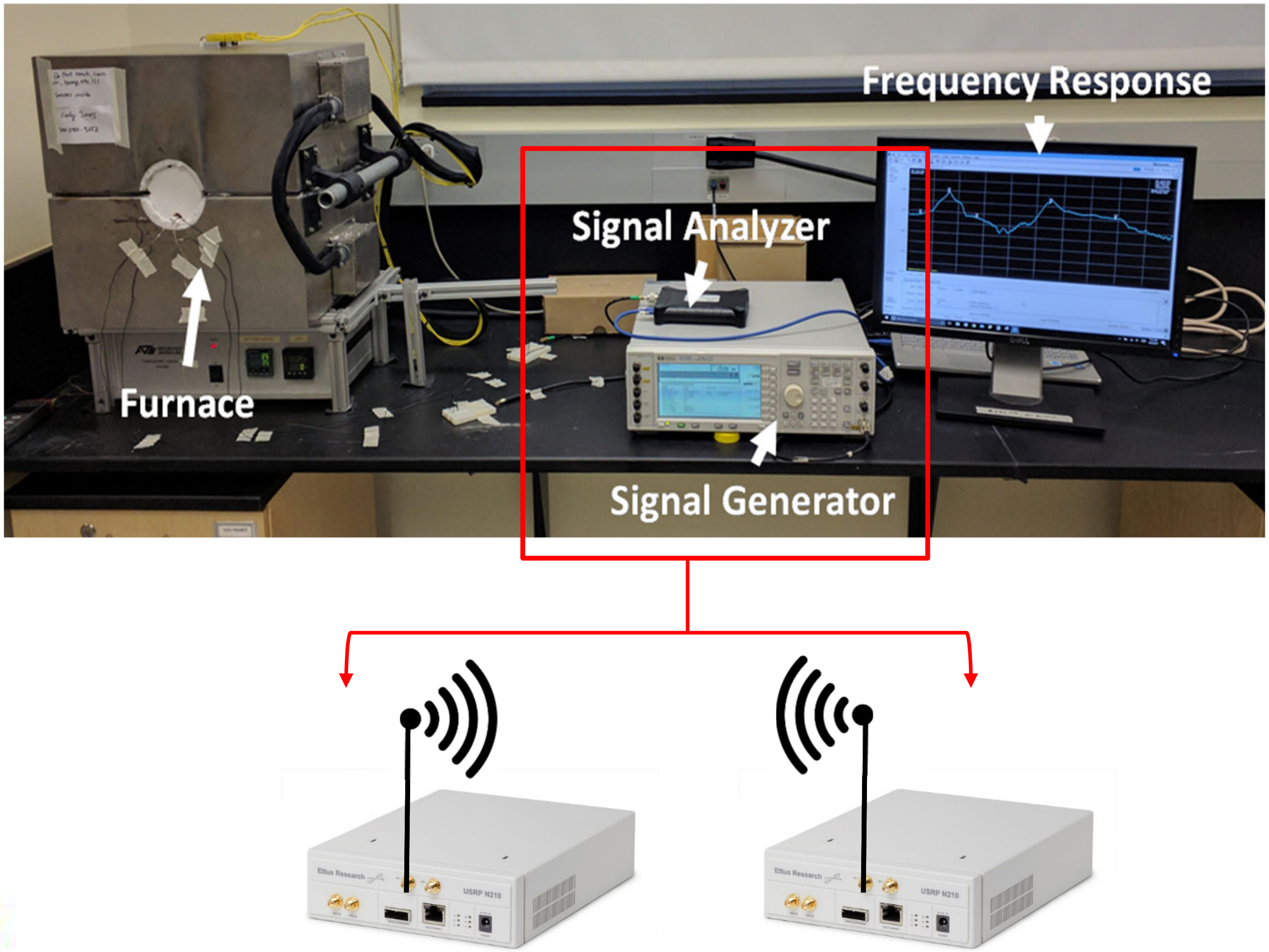


- ❖ **Temperature signatures of the sensor from 500 – 1000°C.**
- ❖ **Optimal window size – 500 : 62 to 68 MHz**
- ❖ **Temperature signatures are unique and distinguishable with a sensitivity of 0.53 kHz/°C.**

Software Defined Radio

- Universal Software Radio Peripheral (USRP) is a software defined radio designed by Ettus research
  - Small, cheap alternative to spectrum analyzers and signal generators
  - Open-source software, existing libraries in open source (GNU Radio), Simulink (Matlab).

USRP Usage in current setup



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