Enabling technologies for surface acoustic wave (SAW) sensors in harsh environments

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NATIONAL ENERGY TECHNOLOGY LABORATORY

Research & Innovation Center

The development of stable high-temperature, harsh-environment films and associated sensors would improve sustainability by increasing the longevity of complex, expensive high-temperature machinery, and will enable reduced overall energy usages and greenhouse gas emissions. This is particularly apropos in fossil fuel applications where safe monitoring of gas emissions is of global concern.

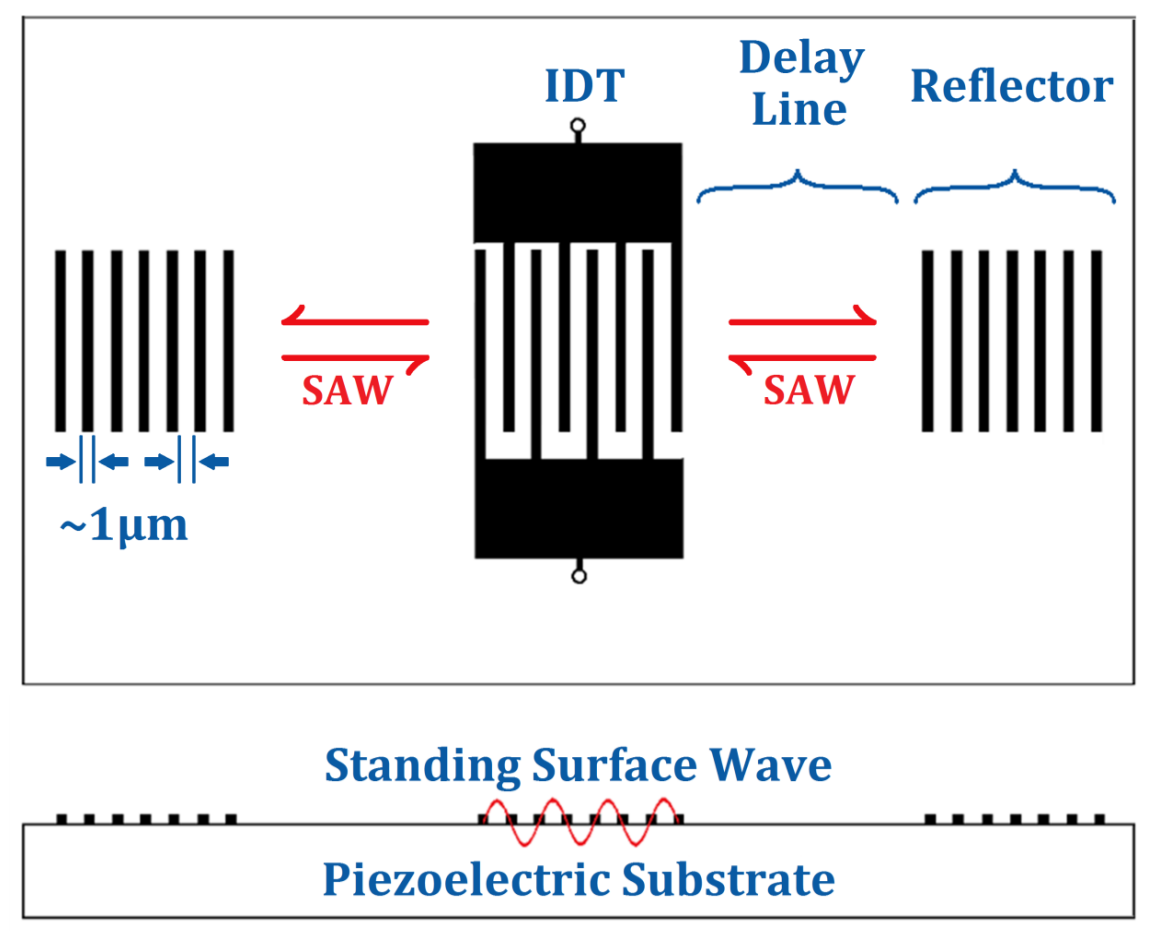
SURFACE ACOUSTIC WAVE (SAW) SENSORS…

are an attractive choice for many harsh-environment energy applications:

- **compact and simple in design**
- **can operate wirelessly & passively (i.e., without use of batteries)**
- **well suited for use at or above 1000 °C**

SAW device electrodes, called **interdigitated transducers (IDTs)**, **create a surface wave on the piezoelectric crystal substrate (and a resonant standing wave at the IDT)** when excited by an AC voltage, via wire contacts or RF signal.

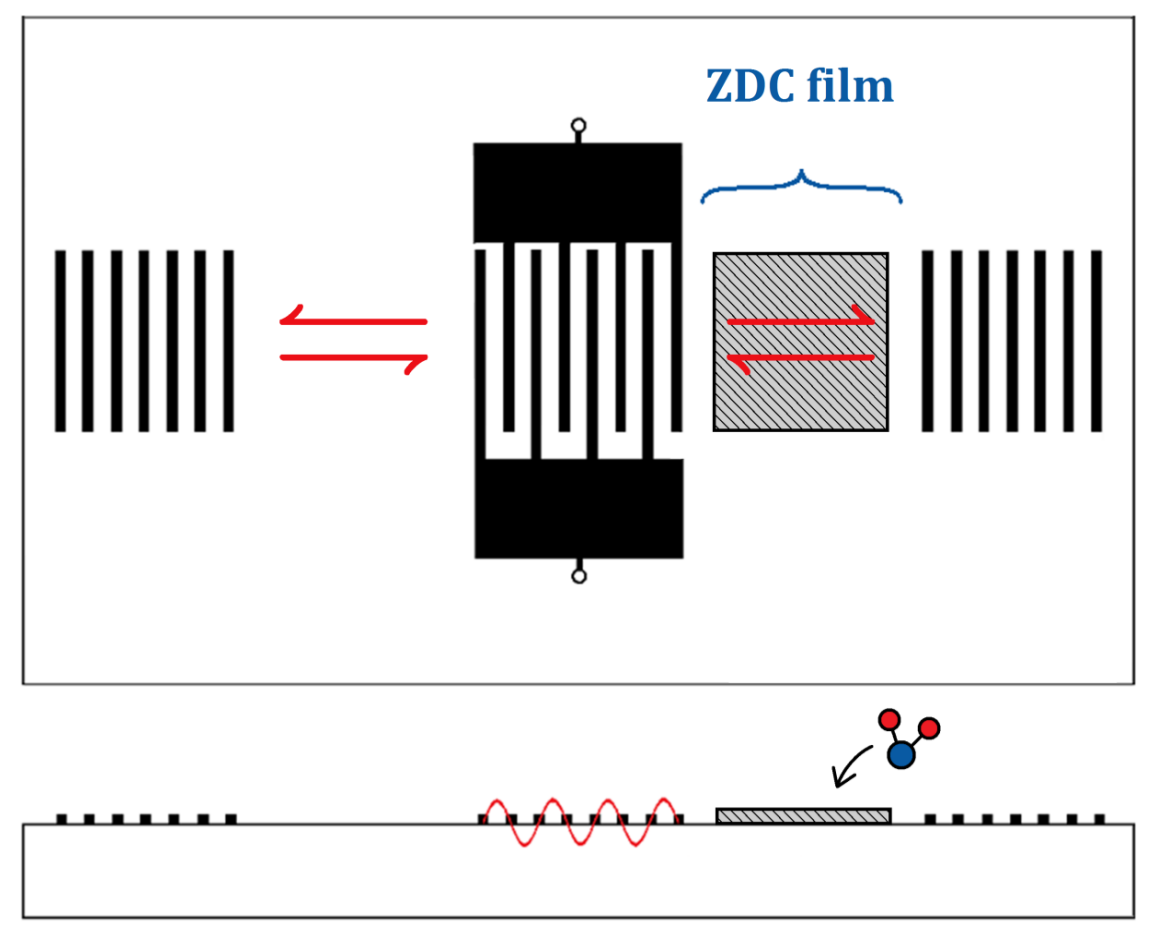
The speed of wave propagation on the crystal surface (and thus the frequency of resonance) is dependent upon parameters such as crystal temperature or vibration. **By monitoring the wave speed (or the resonant frequency, f_R) of the device, these environmental properties can be inferred.**



top

side

SAW sensor for temperature sensing.



Simultaneous gas and temperature sensing.

GAS SENSING MECHANISM:

$$f_R = \text{f}\,(\textit{wave speed}, v_{SAW}) \quad \left[f_R = \lambda_{IDT} / v_{SAW}\right]$$

$$v_{SAW} = \text{f}\,(\textit{film resistivity}, \rho_{film}) \quad \text{(film's ability to dissipate electric surface potentials)}$$

$$\rho_{film} = \text{f}\,(\textit{gas partial pressure}, P_{gas}) \quad \text{(film is oxygen ion conductor)}$$

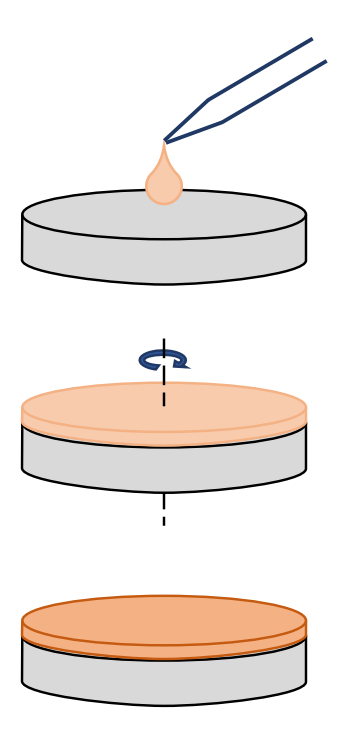
DEVELOPING A STABLE **GAS SENSING LAYER**: SEMICONDUCTING METAL OXIDE THIN FILMS

To alleviate shortcomings with state-of-the-art high-temperature gas sensing layers like ZnO and SnO_2, **ZrO_2-doped CeO_2 thin films** are being explored.

» excellent oxygen storage capacity and high ionic conductivity could improve upon slow sensor response/stabilization times
» reacts catalytically with variety of gases by rapidly exchanging oxygen between the lattice and atmosphere
» minimal temperature dependence of resistivity, which will aid in differentiating partial pressure-induced resistivity changes (Ref. [1])

Synthesis

SOLUTION-BASED PROCESS

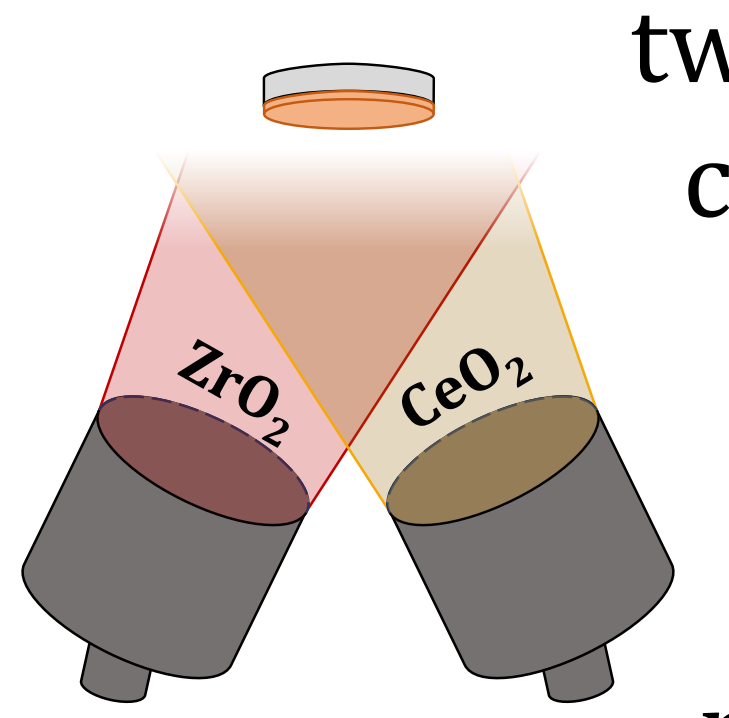


« Ce & Zr salts in solution
« casting
« spinning
« heating

burns off organic solvents leaving thin solid film ($Ce_xZr_yO_z$)

PHYSICAL VAPOR DEPOSITION

- RF magnetron sputtering using two guns, each with a ceramic oxide target



- films grown in ultrahigh vacuum (UHV) resulting in pristine depositions

Characterization

FILM PROPERTIES

- compositional, structural, morphological, electrical
- feedback loop between characterization of as-deposited films and film synthesis procedures to optimize growth parameters for film quality

» XPS, XRD, SEM, Hall effect & electrical resistivity measurements

EFFECTIVENESS OF SENSOR RESPONSE

- determining the films' sensitivity and selectivity to various gases, quantifying the respective resistivity–partial pressure relationships
- characterizing links between film parameters (thickness, roughness, density, resistivity, etc.) and SAW device responses (saturation time constants, device frequency, SAW attenuation & transmittance, etc.)

Processing

LABORATORY REACTOR FURNACES

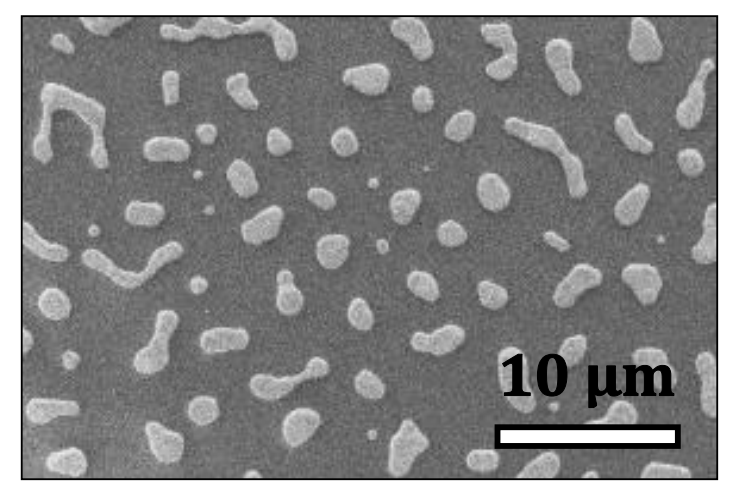
- temperatures/pressures ≥ 800 °C/1000 psi in a one-of-a-kind designated sensor reactor
- configured with various gases relevant for fuel gas streams: H_2, O_2, CO, CO_2, CH_4, N_2

FILM & SENSOR STABILITIES

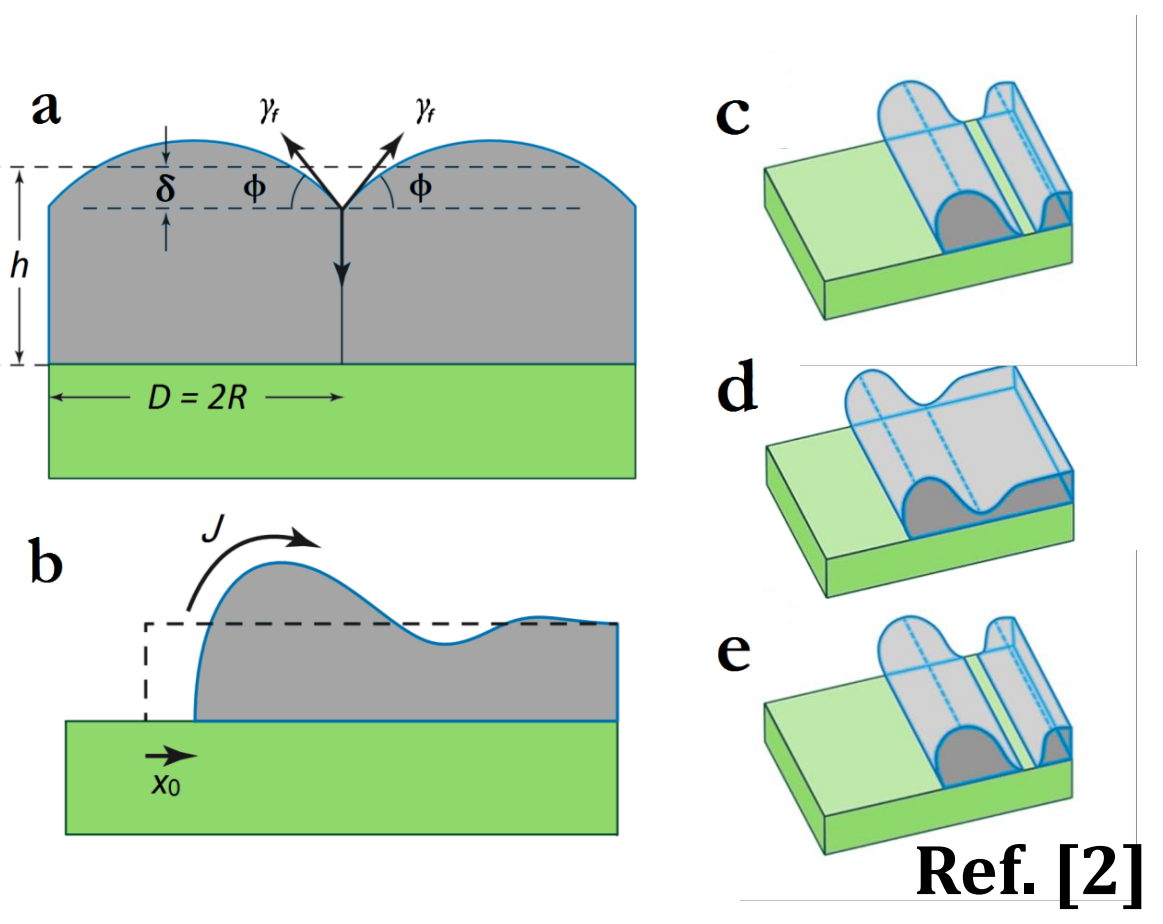
- minimization of substrate–film interdiffusion as well as film cracking and coarsening
- frequency stabilization, low SAW attenuation, stable sensor baselines (no drift), stable time constants, etc.

DEMONSTRATING HIGH-TEMPERATURE STABILITY OF **ELECTRODE MATERIALS**

Stable sensor operation above 800 °C is often limited by electrical instabilities in the thin film electrode material (bondpad contacts and IDTs).
Metallic films can rapidly become electrically insulating by interdiffusion, phase transformations, and morphological roughening/discontinuities.



100-nm Pt film on sapphire substrate after 1 hr at 700 °C



Ref. [2]

This is a heavily studied subject that remains a major technological challenge in vacuum and ambient air conditions.

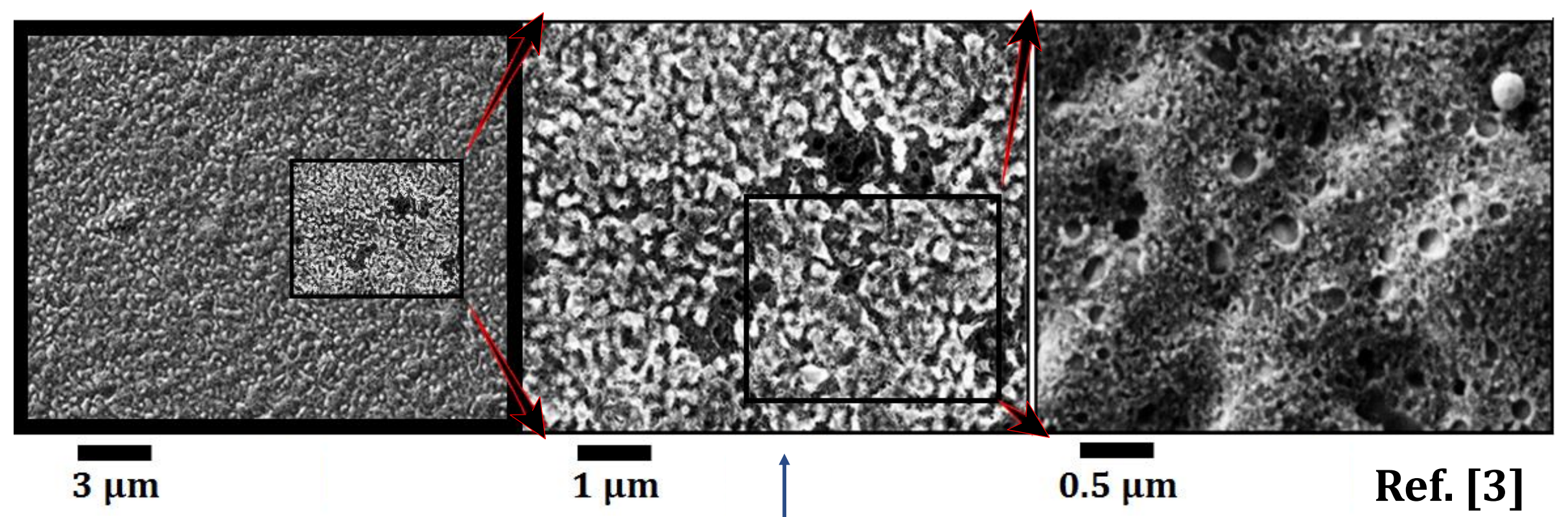
In contrast, **the scientific literature sufficiently lacks studies on high-temperature electrical stability of metallic films in non-ambient, non-vacuum conditions** like the chemically aggressive and/or pressurized atmospheres common to many fossil energy applications (solid oxide fuel cells, gasifiers, gas turbines, etc.).

University Partnerships & Collaborations

Several groups currently funded under U.S. DOE UCR grants, like **The University of Maine** & **The University of Connecticut**, are strong leaders in the research and development of high-temperature-stable thin film materials specifically tailored for operation on SAW sensor devices.

UMaine, for example, has demonstrated electrode stability in air at new temperatures by way of **Pt-ceramic nanocomposite thin films and films with multilayer architectures**.

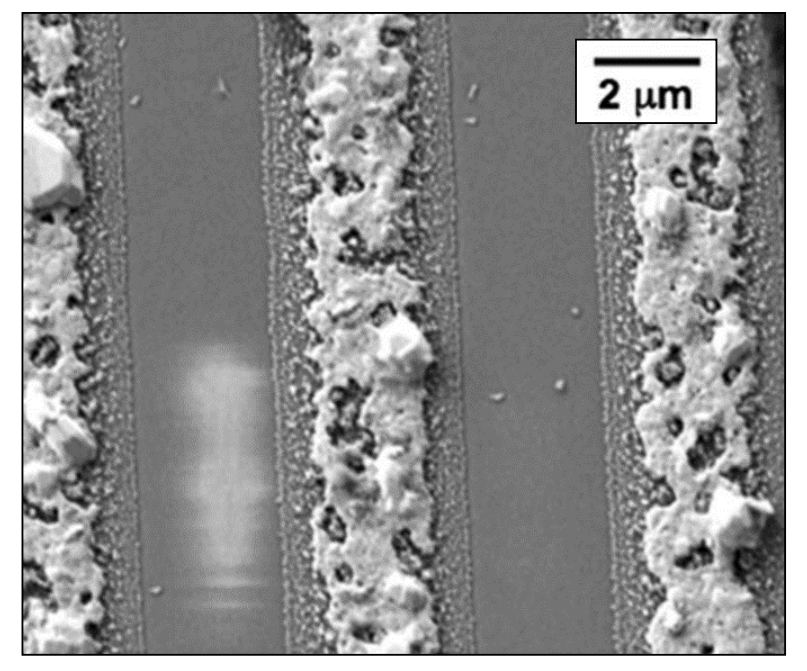
nanocrystalline Pt network stabilized within amorphous SiO_2 matrix



Ref. [3]

backscatter electron image: "bright" material is Pt, "dark" is SiO_2

Pt-Rh/HfO_2 nano-composite IDTs



Long-term stable in air up to 900 °C

Ref. [4]

[1] N Izu *et al.*, Sensors and Actuators B 108 (2005) 216.
[2] CV Thompson, Annu. Rev. Mater. Res. 42 (2012) 399.
[3] RT Fryer *et al.*, PhD thesis, University of Maine (2016).
[4] SC Moulzolf *et al.*, Microsyst. Technol. 20 (2014) 523.

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