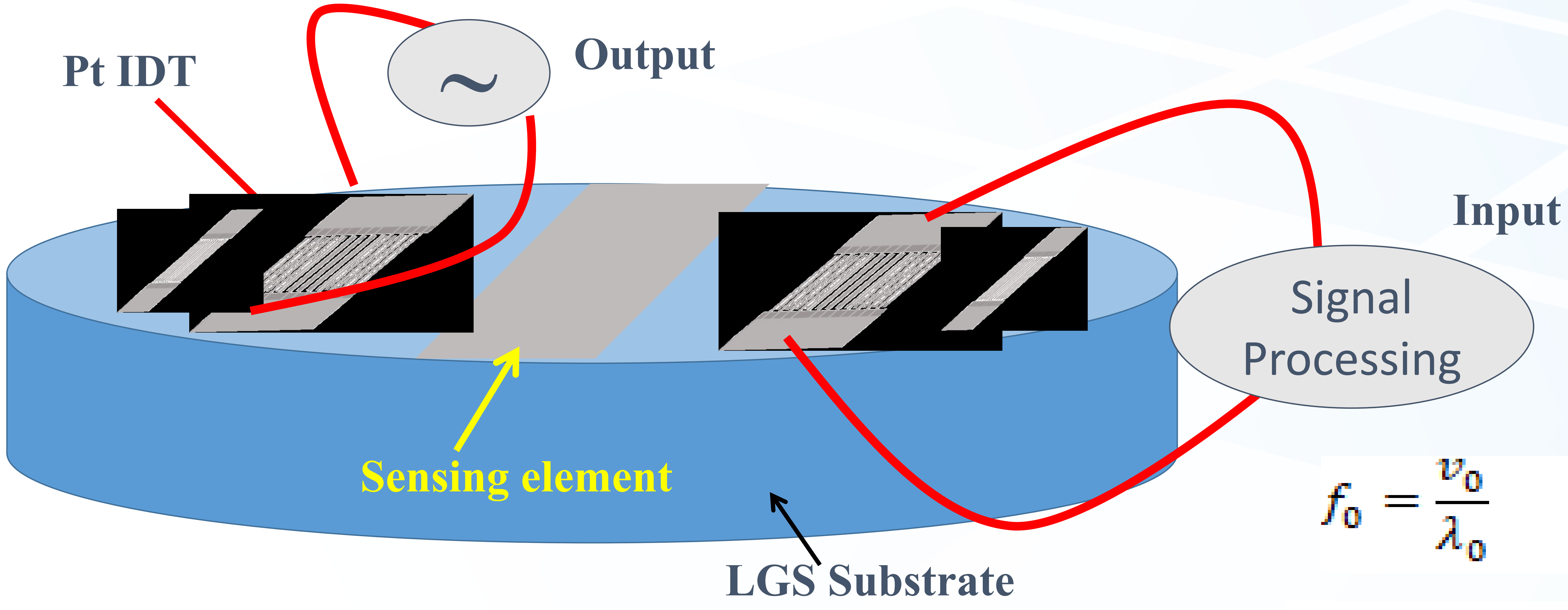
High temperature CO_2 sensing characteristics of Langasite based SAW sensor and Langasite MEMS micro-cantilever gas sensor

Mass loading effect in SAW sensor



$$f_0 = \frac{v_0}{\lambda_0} \qquad (1)$$

$$\frac{\Delta v}{v_0} = -\frac{\omega v_0 \rho_s}{4}\left(\frac{v_{x0}^2}{\omega P} + \frac{v_{y0}^2}{\omega P} + \frac{v_{z0}^2}{\omega P}\right) \qquad (2)$$

Δ**v** is the change in the SAW velocity, ω is the angular resonant frequency ($=2\pi f_0$),

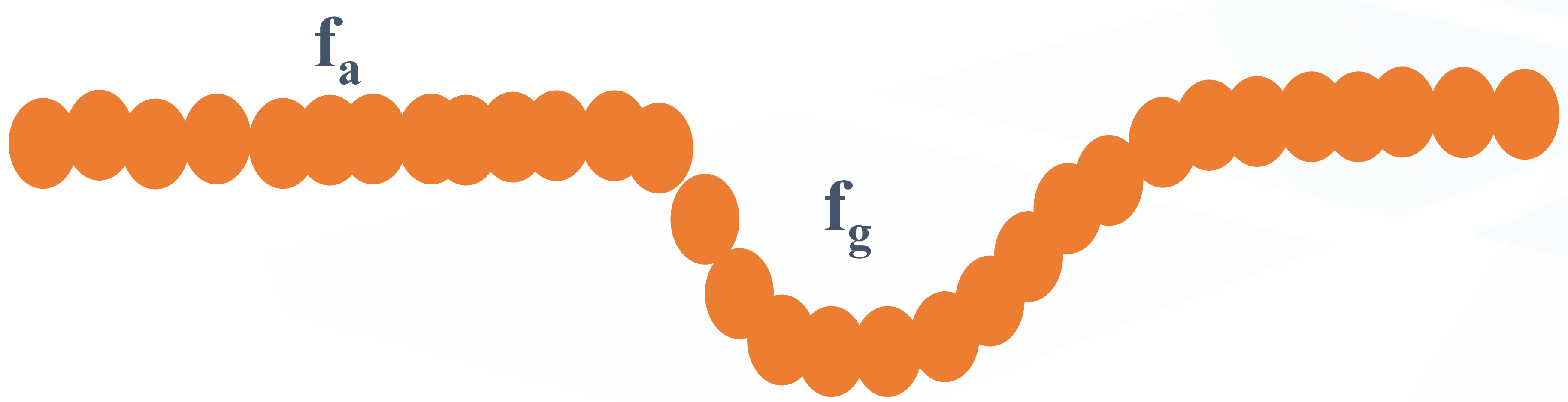
P is the power density

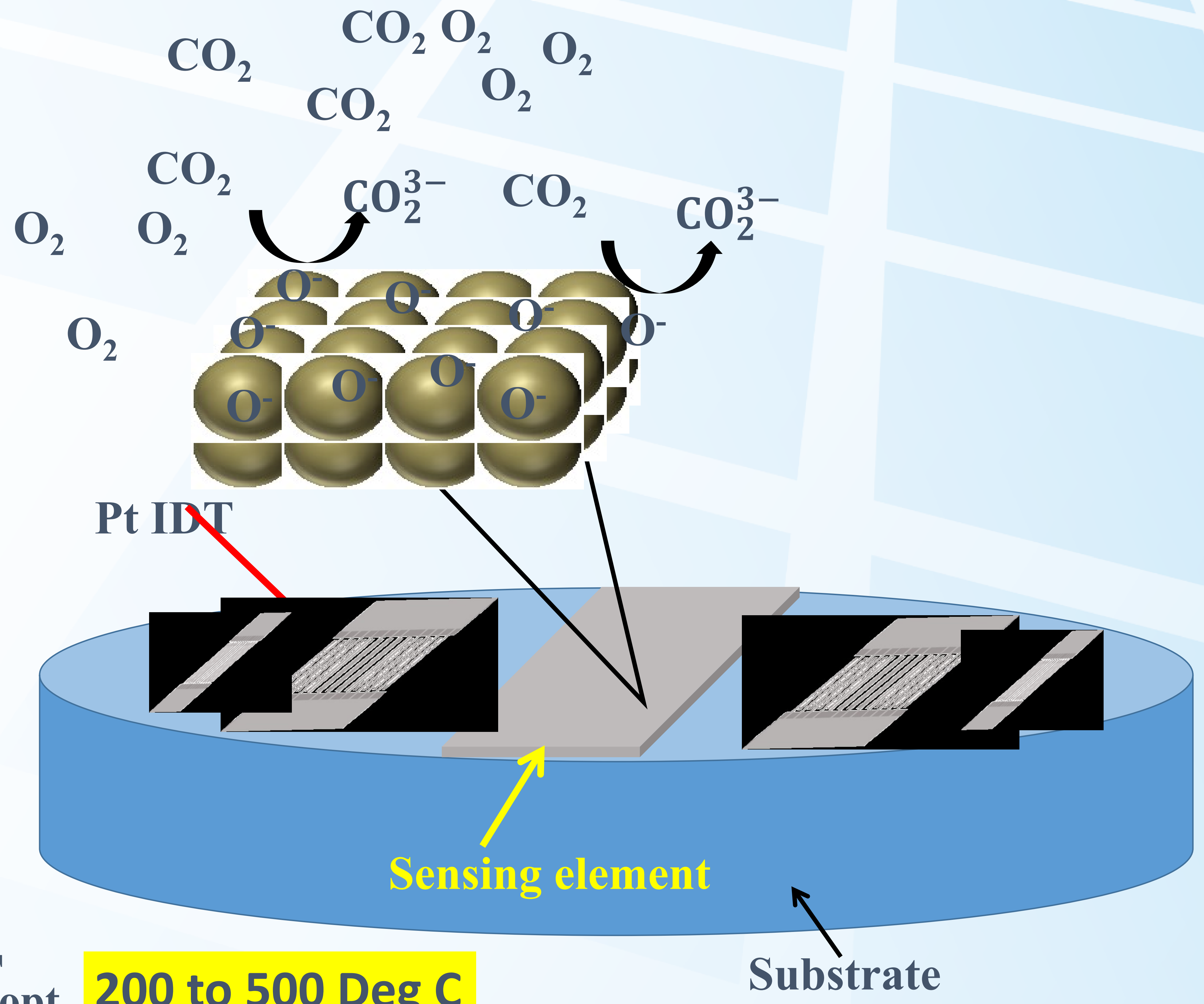
v_{x0}, v_{y0}, v_{z0} are the SAW particle velocity at the surface with respect to different directions, respectively.

ρ_s is the surface mass density,

$v_{xo}^2/\omega P$ is constant, depends on the materials only

Sensing Mechanism for SAW sensor



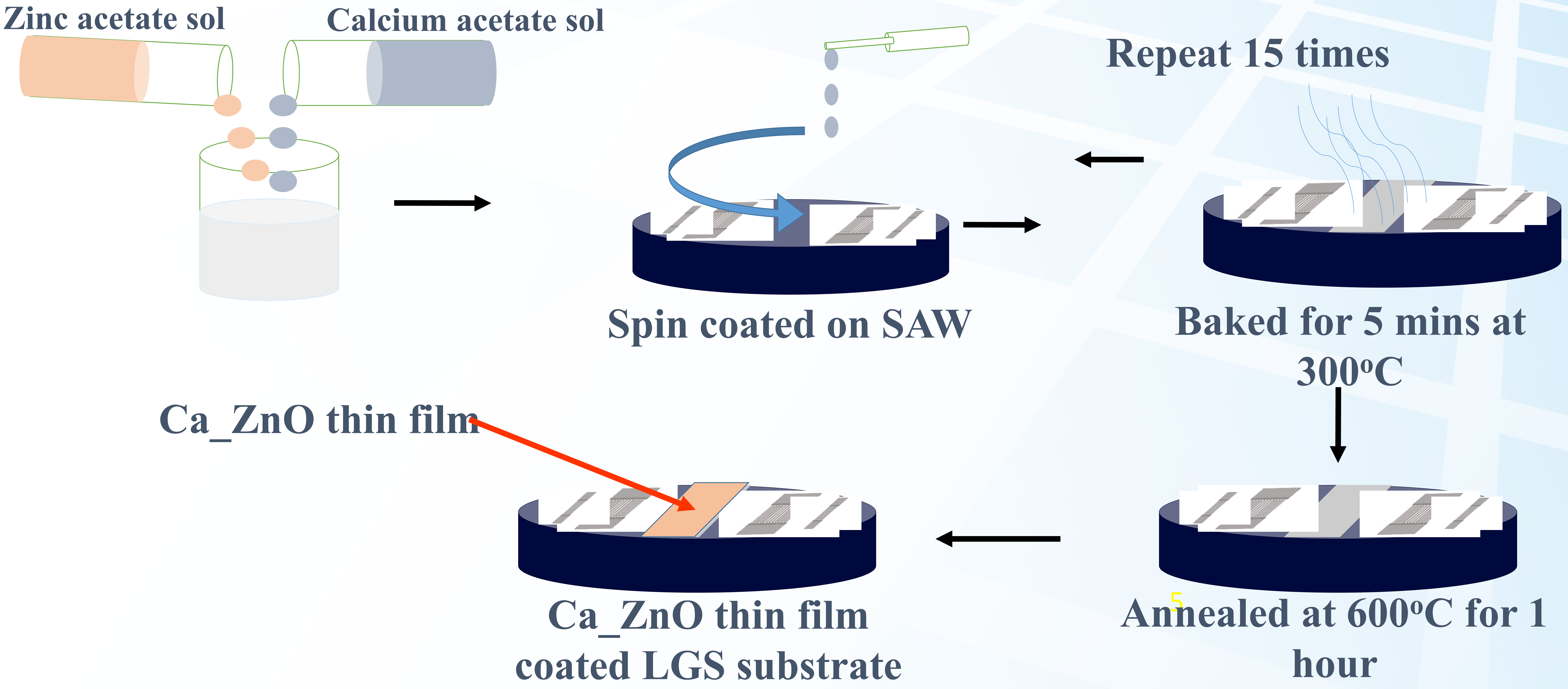


Response (S) =$(f_a\text{-}f_g)/f_a$

At T_{opt} 200 to 500 Deg C

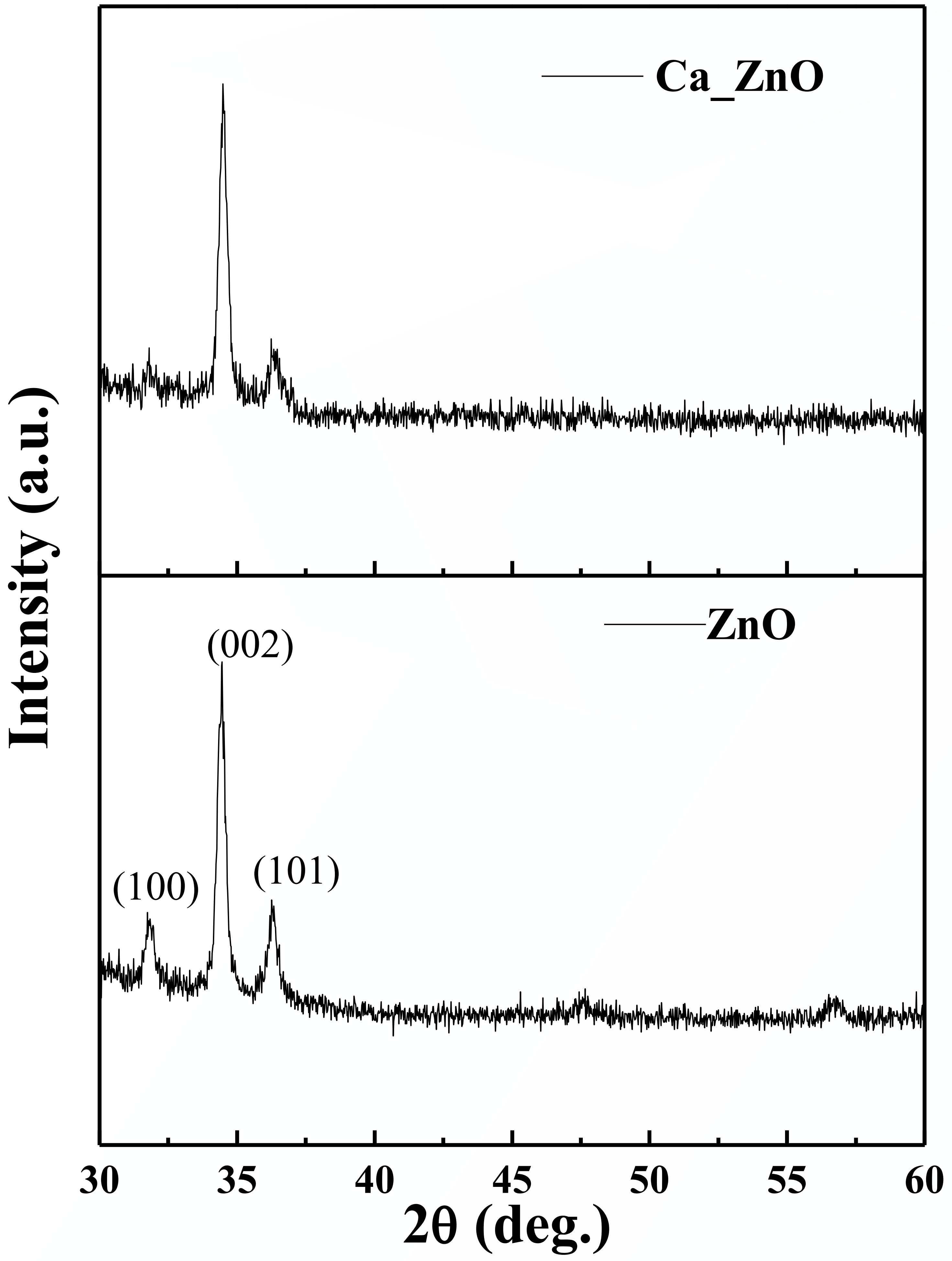
Fabrication process

Synthesis of Calcium doped ZnO thin film

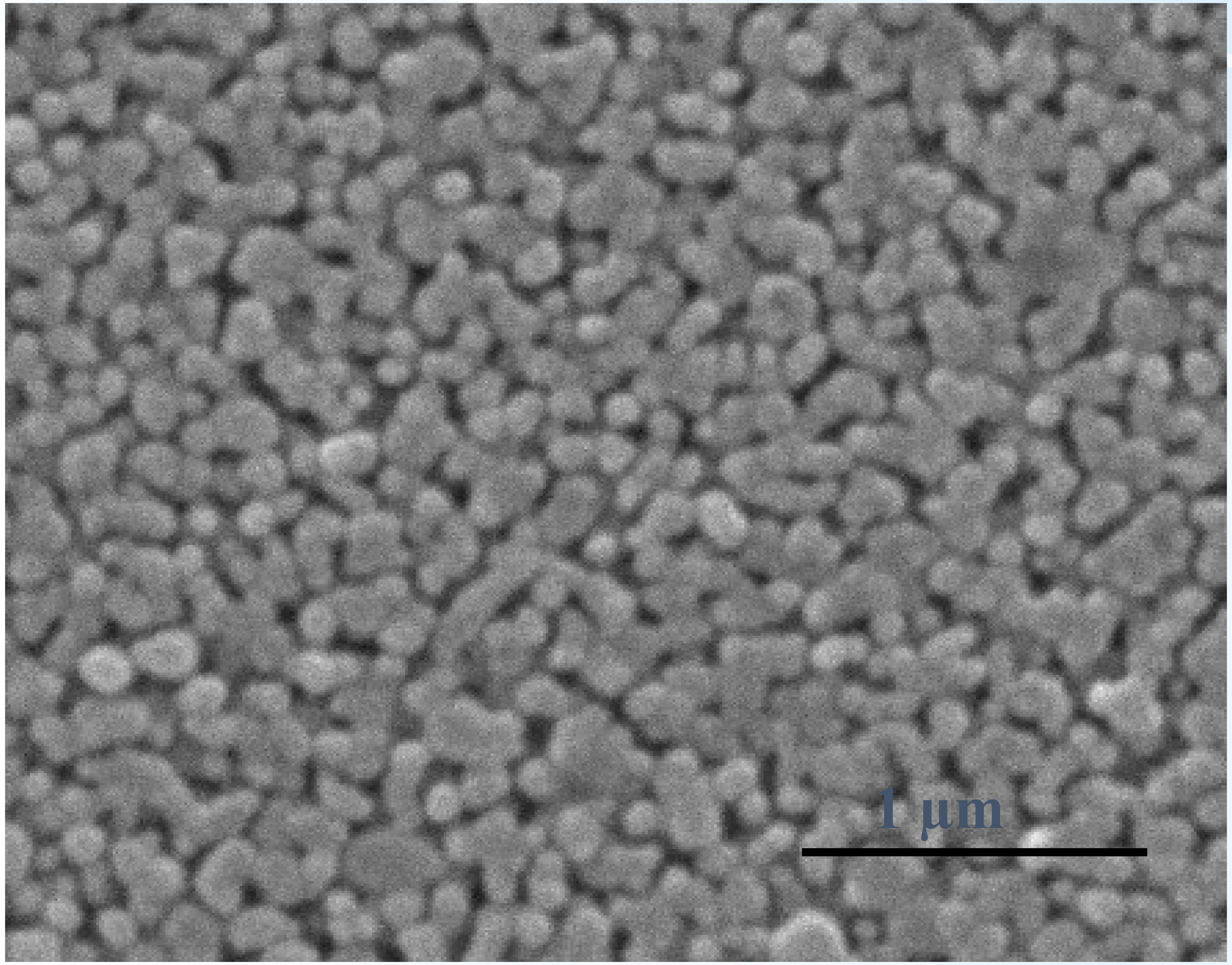


Phase formation and microstructure of Ca_ZnO thin film

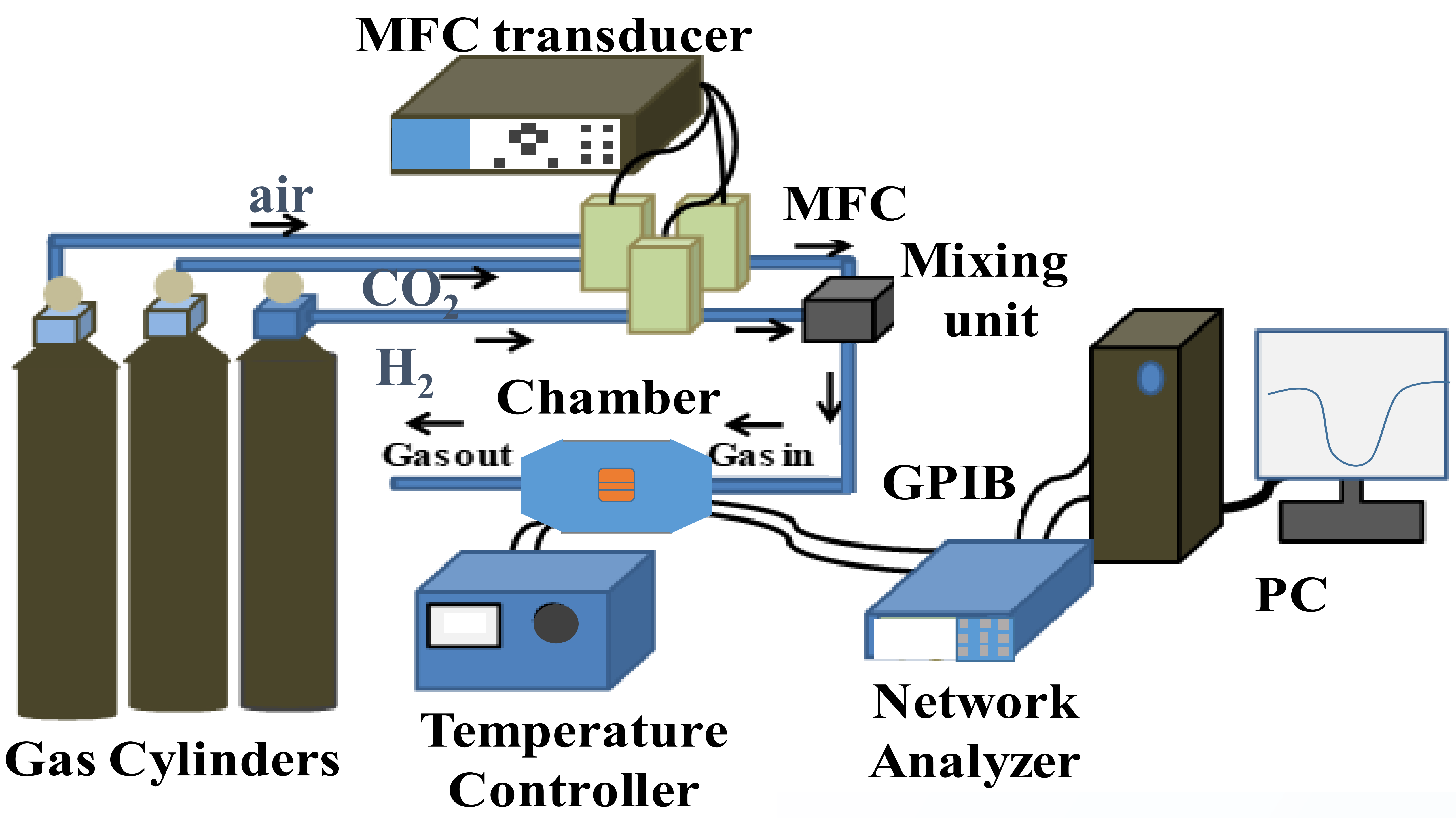
XRD

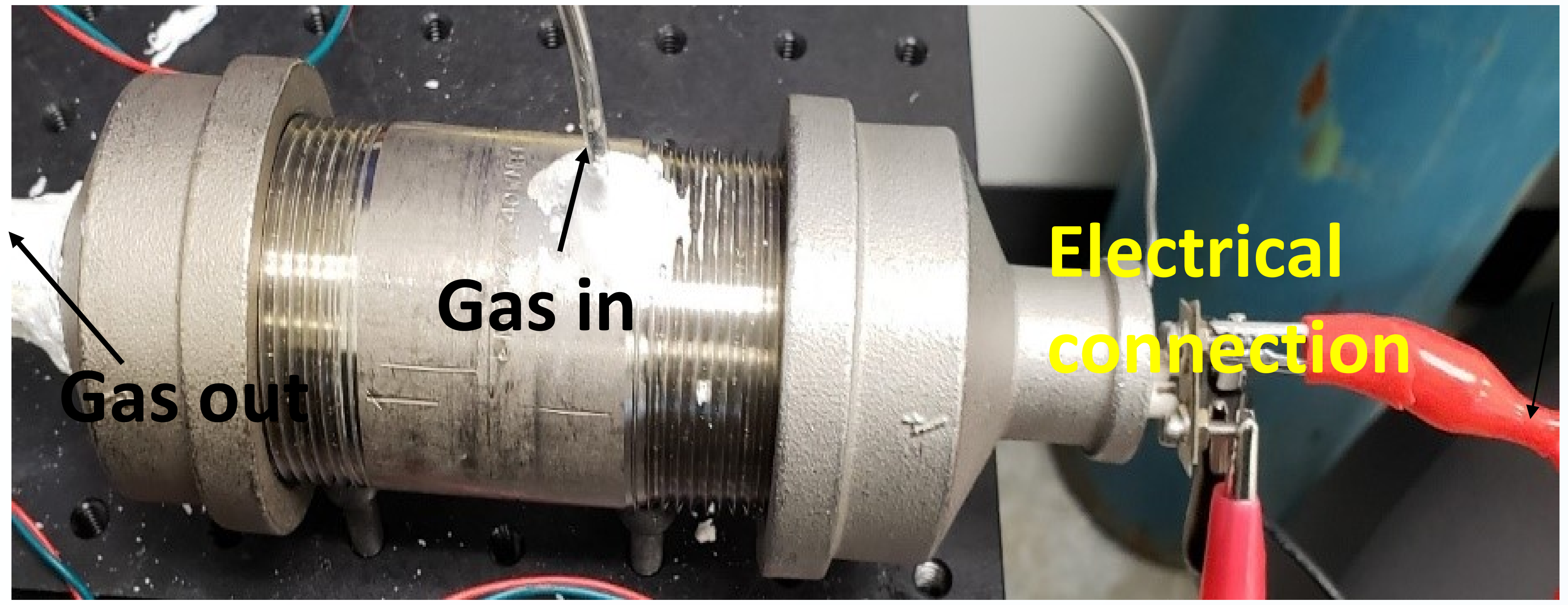


SEM Microstructure of Ca_ZnO thin film



experiment setup

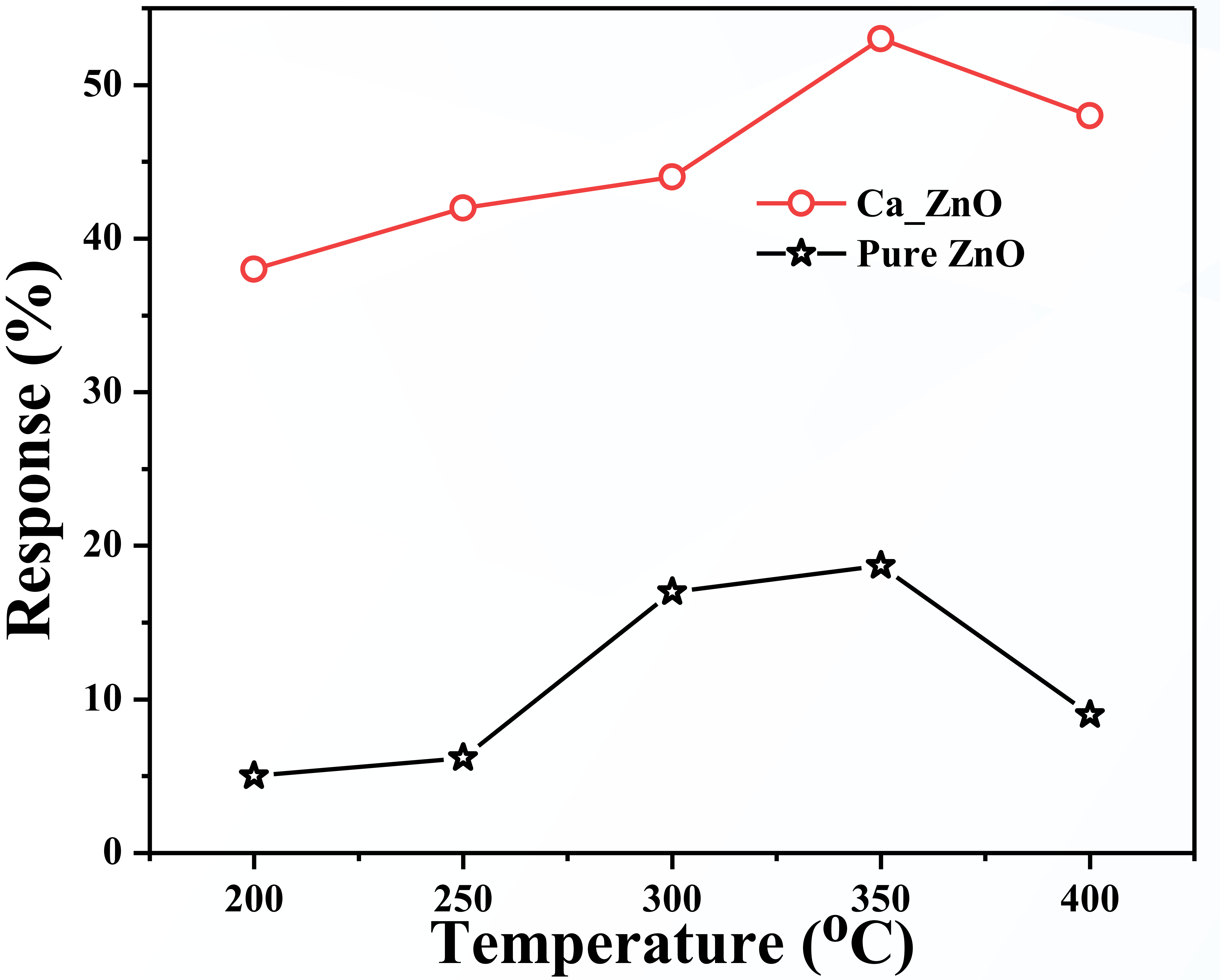




Sensing Unit

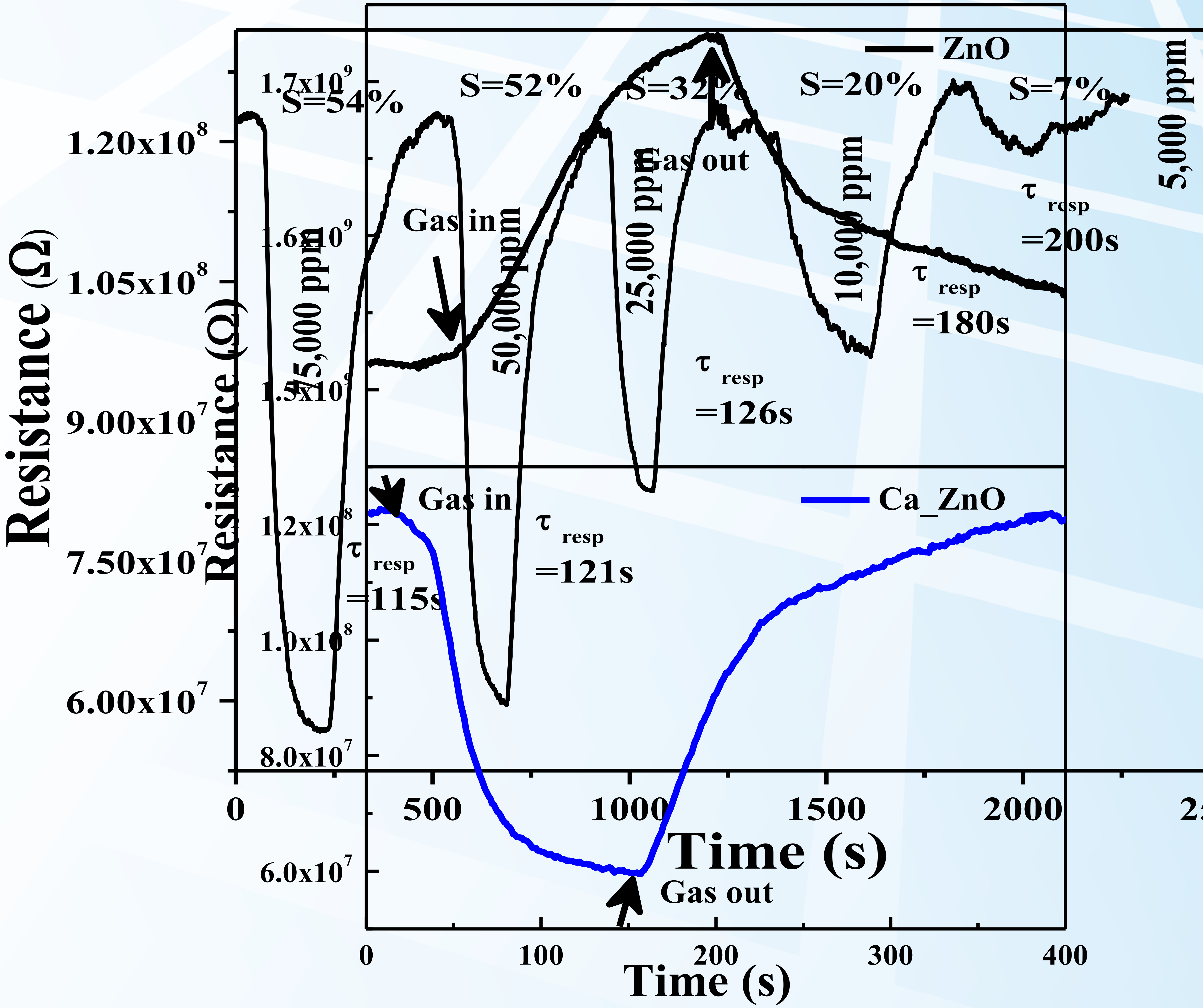
CO_2 sensing of chemo-resistive Ca_ZnO thin film

Temperature effect on 50,000 ppm CO_2 response

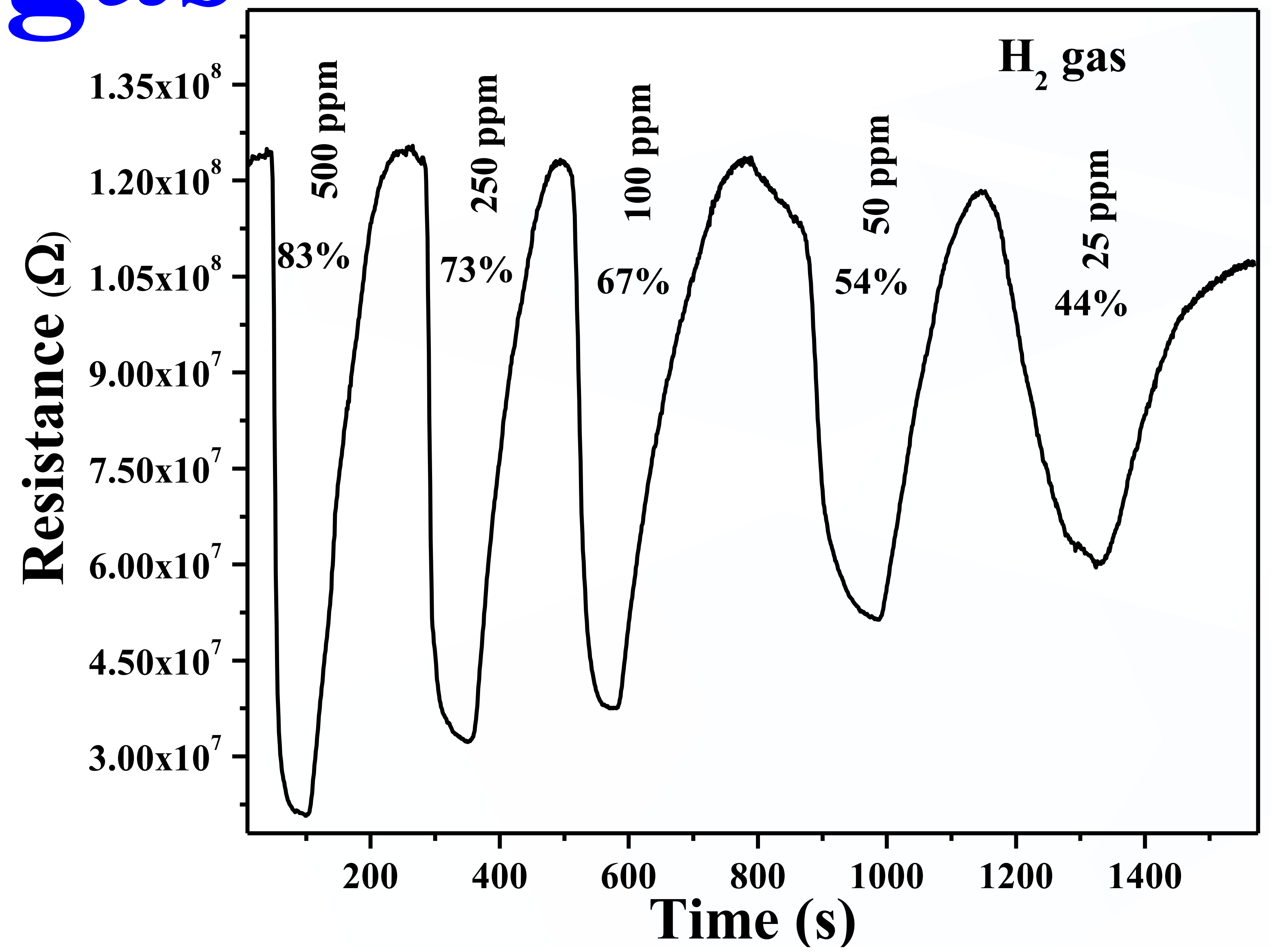


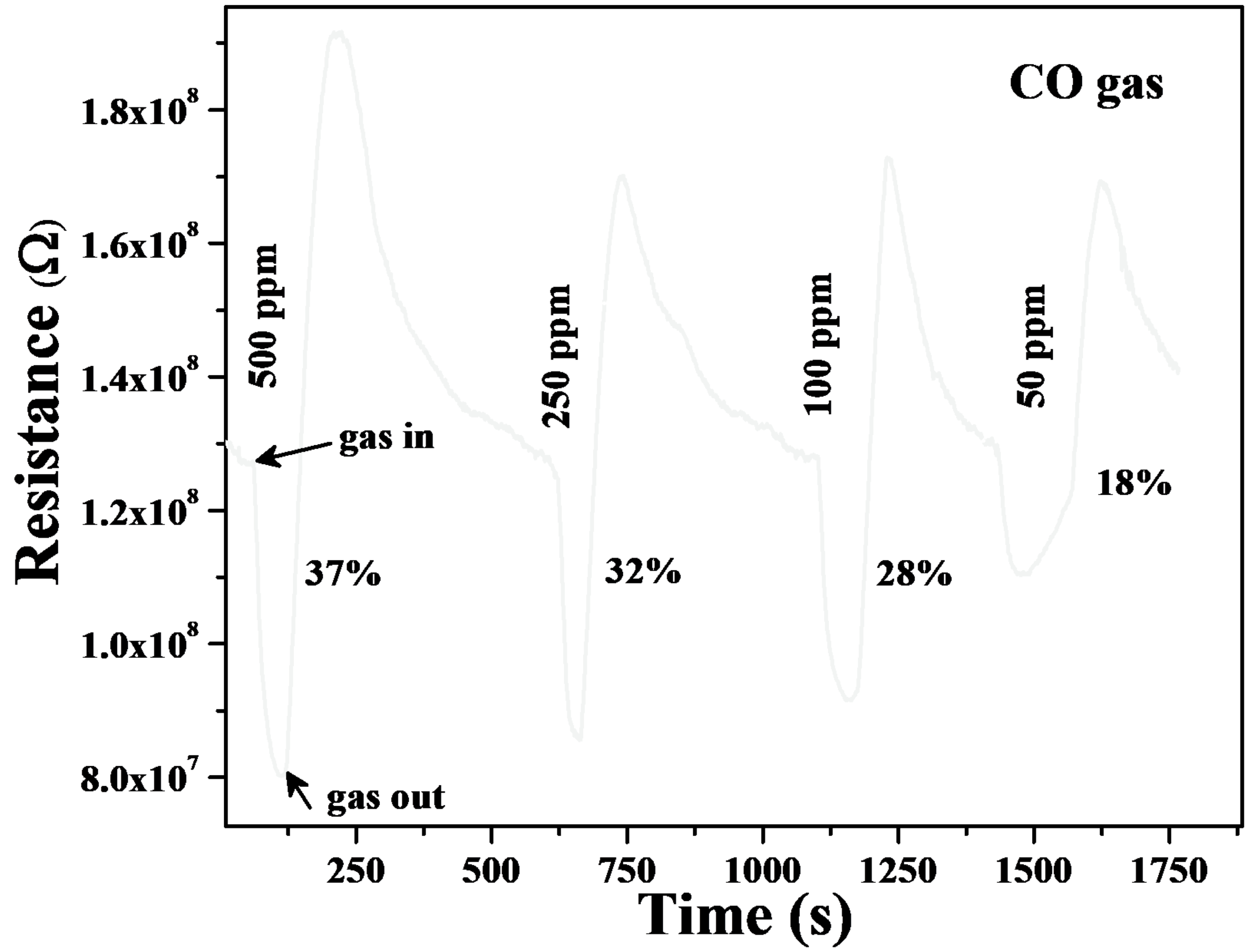
Concentration dependence CO_2 response in Ca_ZnO thin film

CO_2 sensing in Pure ZnO and Ca_ZnO thin film



Cross-sensitivity of CO_2 in H_2 and CO gas



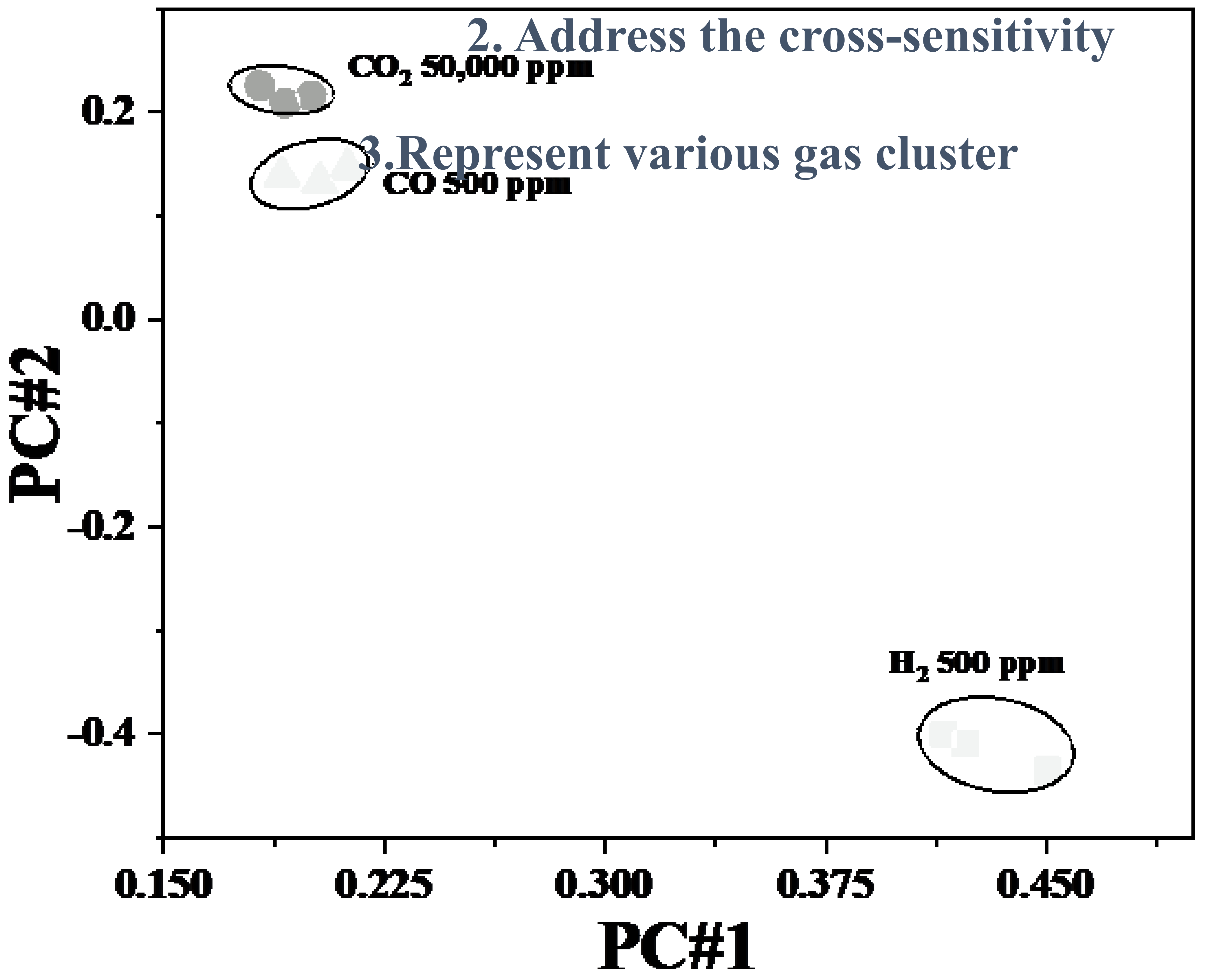


Principal component analyses (PCA)

1.Unsupervised pattern recognition technique

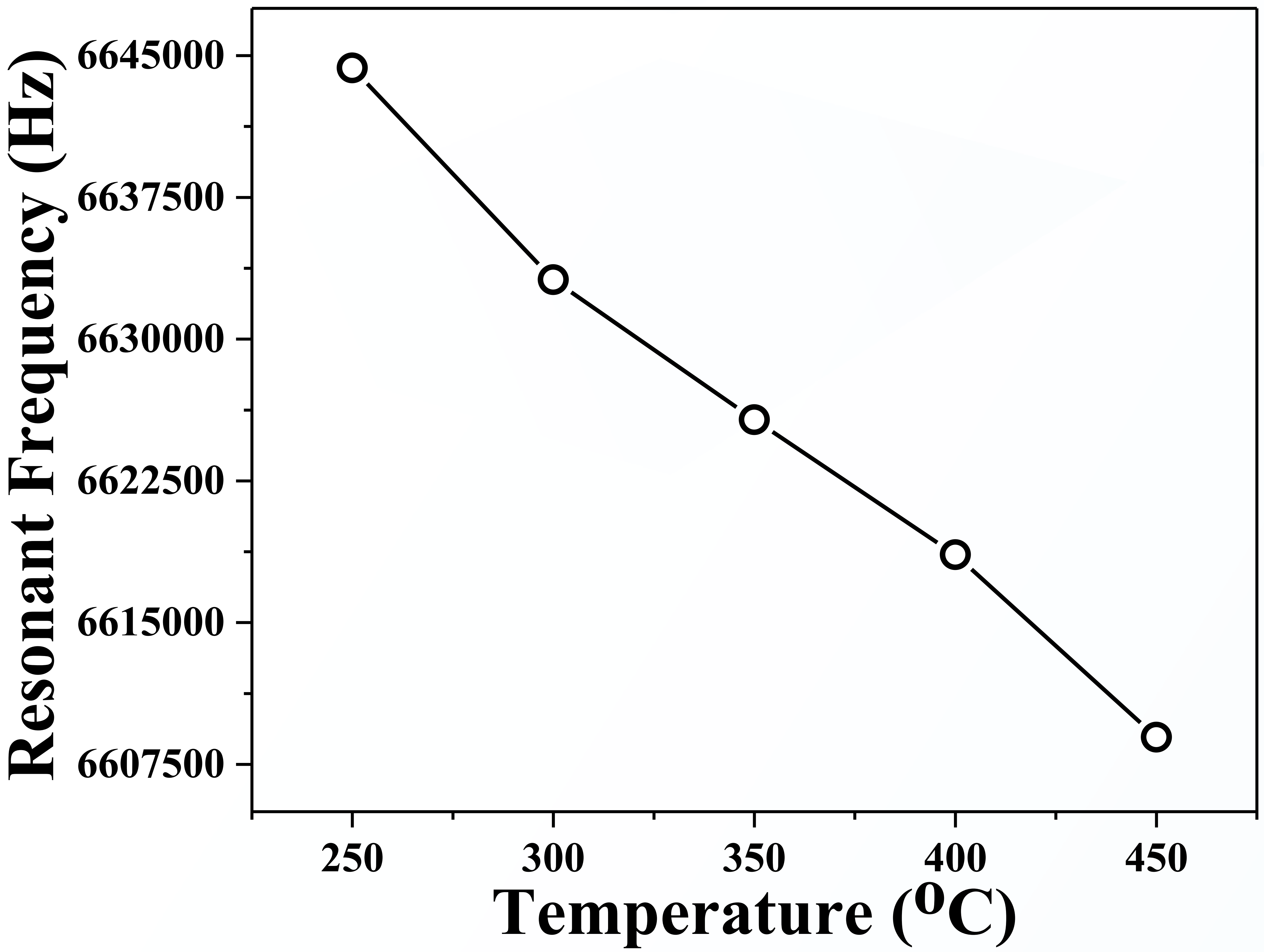
2. Address the cross-sensitivity

3.Represent various gas cluster

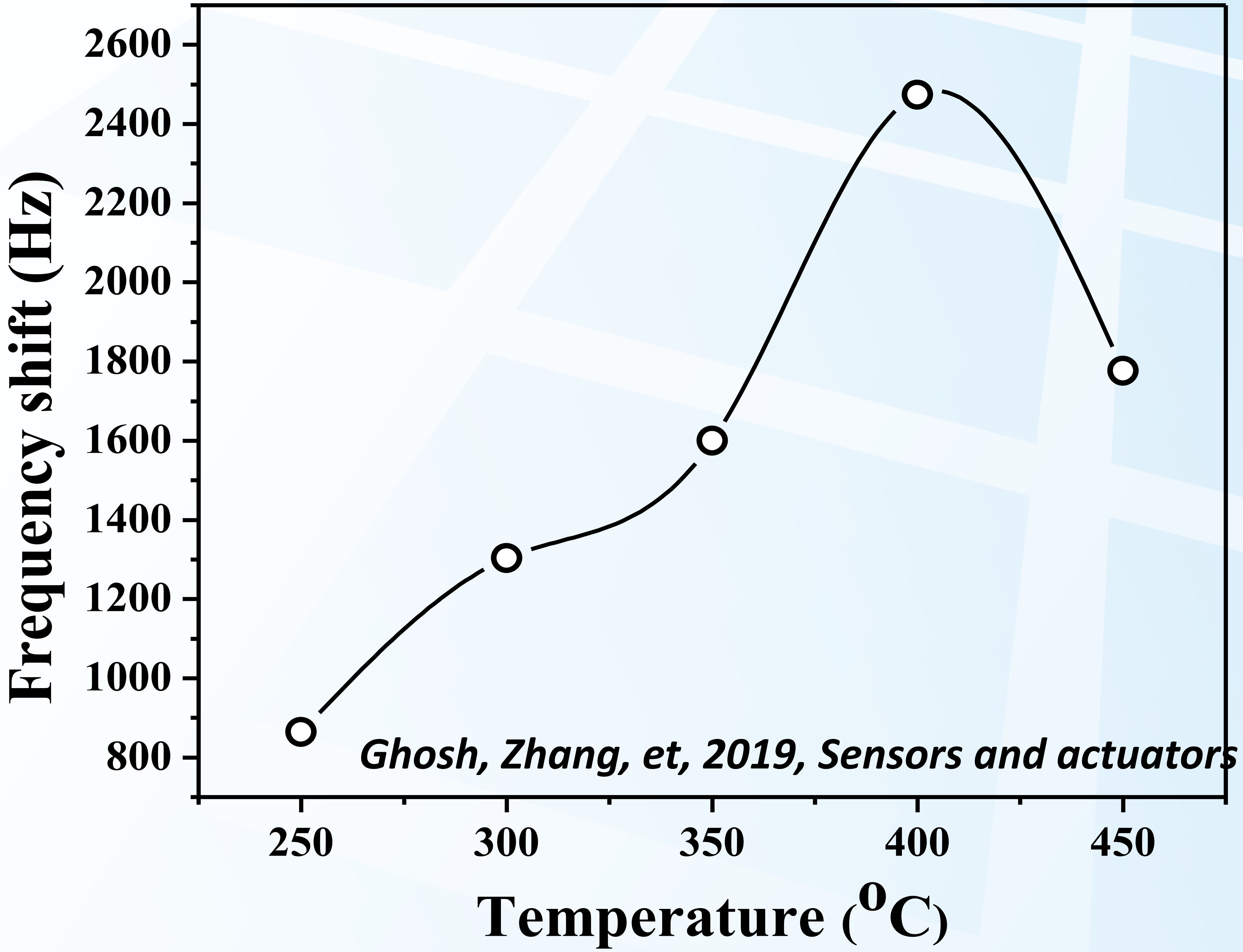


CO_2 sensing of Ca_ZnO thin film coated LGS SAW sensor

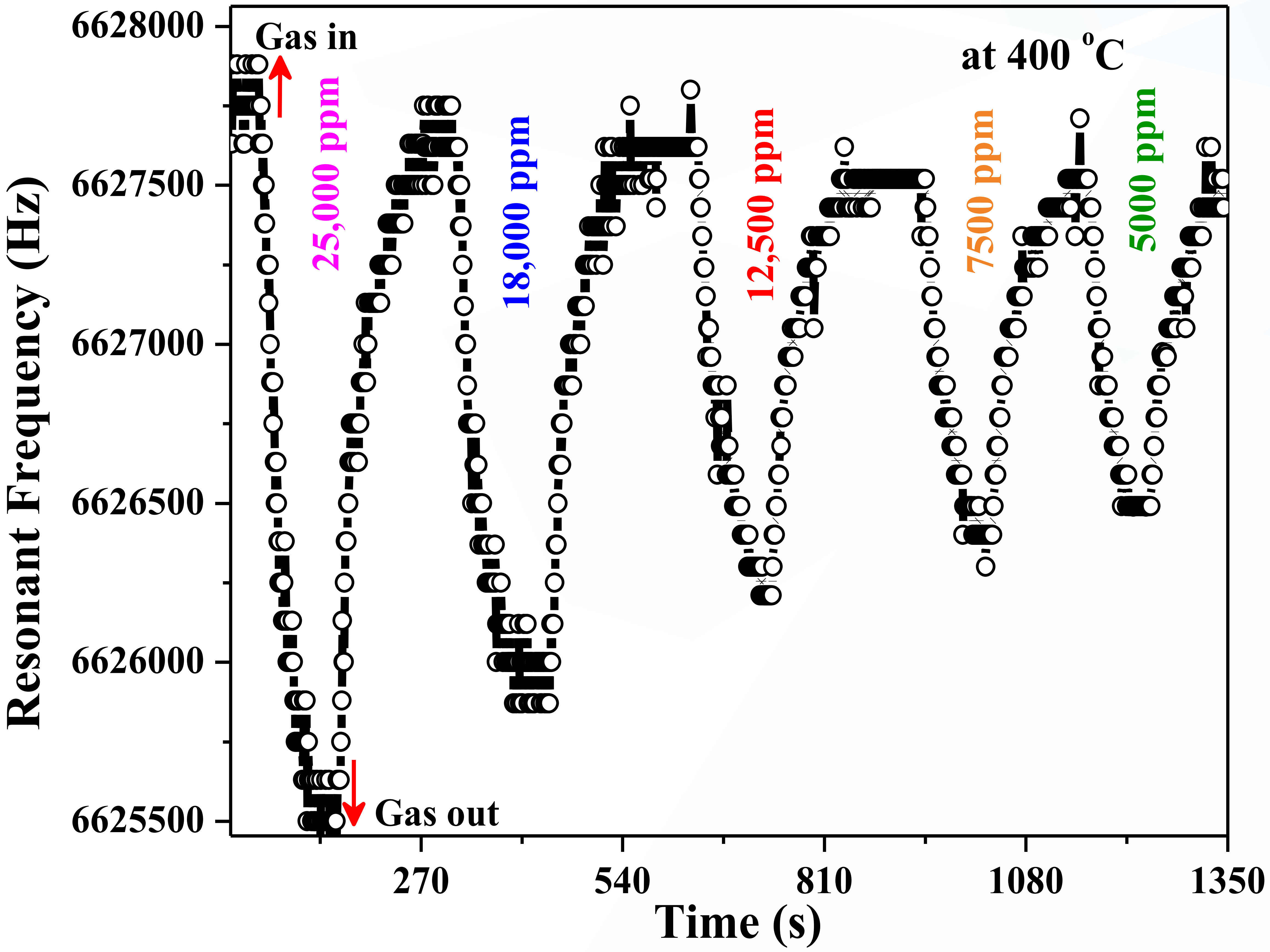
Temperature effect on resonant frequency



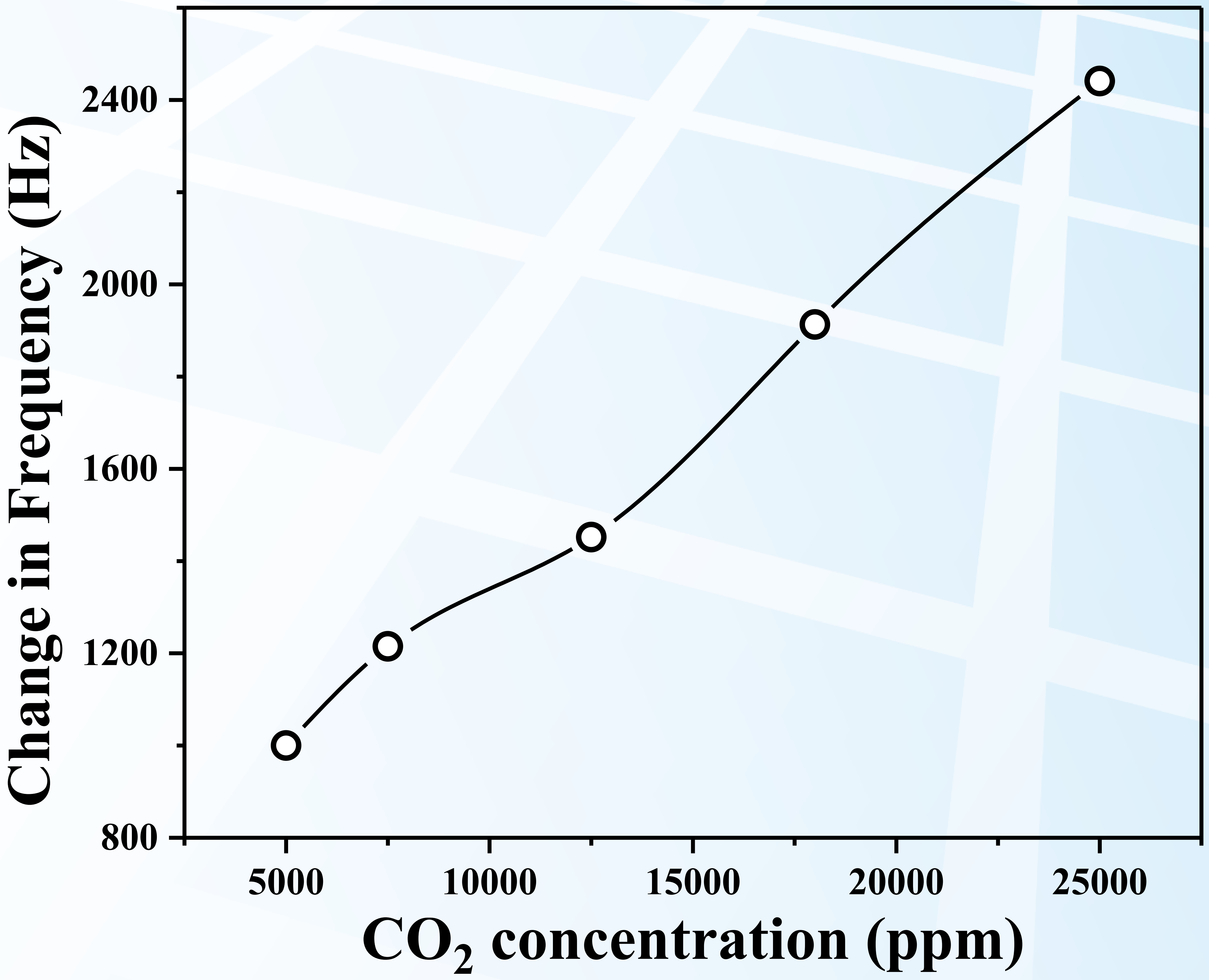
Temperature dependent CO_2 sensing



variation



Gas in
Gas out
at 400 °C
25,000 ppm
18,000 ppm
12,500 ppm
7500 ppm
5000 ppm
Resonant Frequency (Hz)
6628000
6627500
6627000
6626500
6626000
6625500
270
540
810
1080
1350
Time (s)



Change in Frequency (Hz)
2400
2000
1600
1200
800
5000
10000
15000
20000
25000
CO_2 concentration (ppm)

Comparison of High Temperature CO_2 sensors

Materials	Synthesis Method	Operating temperature	Optimum temperature	gases	Response(%)	Cross-sensitivity	Reference
Calcium/aluminum co-doped zinc oxide (ZnO:(Ca,Al)) nanoparticles (NPs),	Wet chemical	200 to 450 ^oC	200 ◦C (ZnO:Ca3Al1 under UV) 300 ^oC (ZnO:Al1% Ca 3%) 450 ^OC (ZnO:Ca5)	CO_2 (0.25% to 5%)	~4.5(R_O/R: ZnO:Al1% Ca 3%) ~4 (UV)	NA	Dahiri et al. SNB, 2017, 239, 36.
pure ZnO and La-loaded ZnO (powder)	hydrothermal method	250 to 400^oC	400 ^oC .	CO_2 (5000 ppm)	65% ($\Delta R/R_a$) (50 at% La-loaded ZnO)	Not performed	Jeong et al. SNB, 2016, 229, 288
SnO_2 thick film by coating lanthanum oxide	Wet chemical	400 to 1200^oC	1000 ^oC	CO_2 (5000 ppm)	1.375 (R_a/R_g)	Not performed	Kim et al. SNB, 2000, 62, 61
1.Ca doped ZnO thin film (chemo-resistive). 2.Ca_ZnO coated LGS based SAW sensor.	Wet chemical	200 to 450^oC	350 ^oC for Chemo-resistive 400^oC for SAW	CO_2 (5000 to 75,000ppm)	52% ($\Delta R/R_a$) for 50,000 ppm. (Chemo-resistive) Δf = 2400 Hz (SAW)	Cross-sensitive	Present work

Comparison with the commercial CO_2 sensors

Method	Concentration range	Response time	Temperature range	Reference
NDIR type	0 to 40,000 ppm (accuracy 400-10,000 ppm)	20 s	40-70 ^oC	**Sensirion**
NDIR type	300 -5000 ppm	2 min	0-50^oC	**Figaro**
NDIR type	0 to 100,000 ppm	2 min	25^oC	**Vernier**
MOX and SAW (Ca_ZnO coated LGS)	0 to 75,000 ppm	~115 sec (MOX) ~30 sec (SAW)	200 to 450 ^oC	Present work

Conclusion/ Future Work

Conclusion

- Ca_ZnO thin film successfully deposited on quartz and LGS substrate.
- Higher response is achieved for a wide concentration of CO_2 gas.
- Cross-sensitivity is addressed using PCA analyses.
- Optimum CO_2 response is obtained at 350 and 400°C for metal oxide and SAW sensors respectively.
- CO_2 sensing enhanced due to catalytic effect of calcium.

Future works

- CO_2 sensing and its cross-sensitivity in various mixed gas environment at high operating temperature should be investigated further.

ZnO nanorods enhanced Langasite MEMS micro-cantilever gas sensor

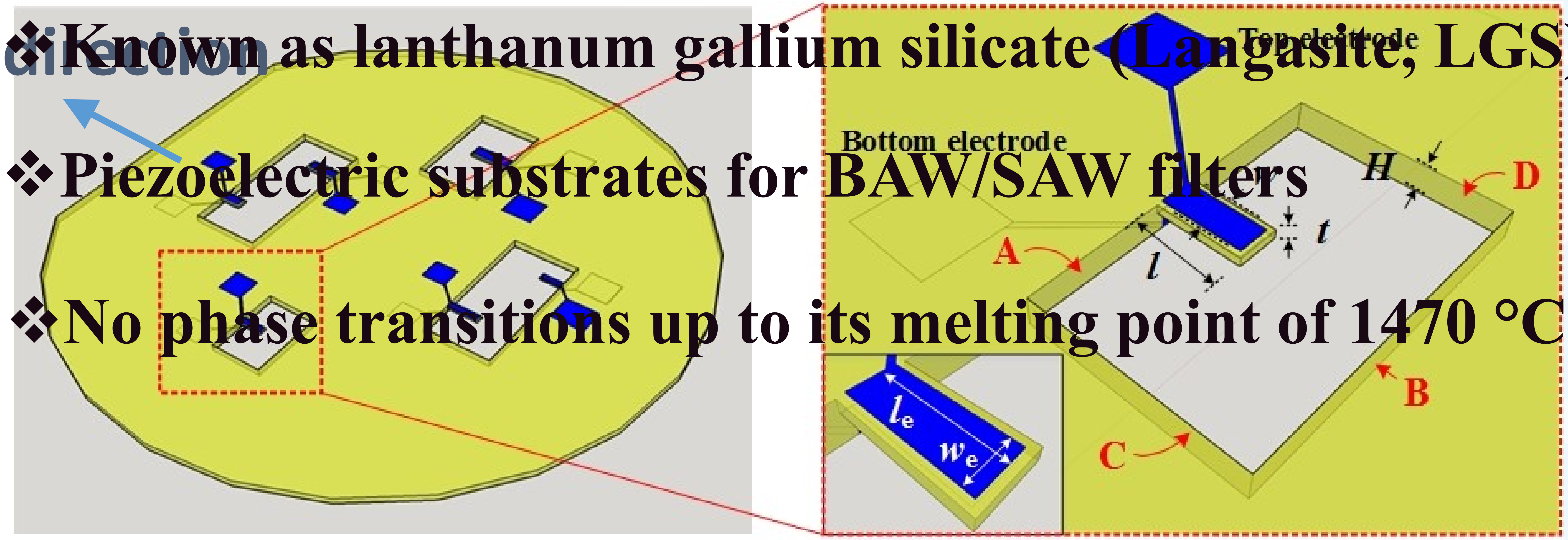
Thickness shear mode vibration of LGS MEMS

Y-cut thickness shear mode Langasite (LGS)

❖Known as lanthanum gallium silicate (Langasite, LGS)

❖Piezoelectric substrates for BAW/SAW filters

❖No phase transitions up to its melting point of 1470 °C



t=thickness of cantilever,

w=width of cantilever,

l=length of cantilever,

h=thickness of the substrate,

w_e=width of electrode, and

l_e=length of electrode

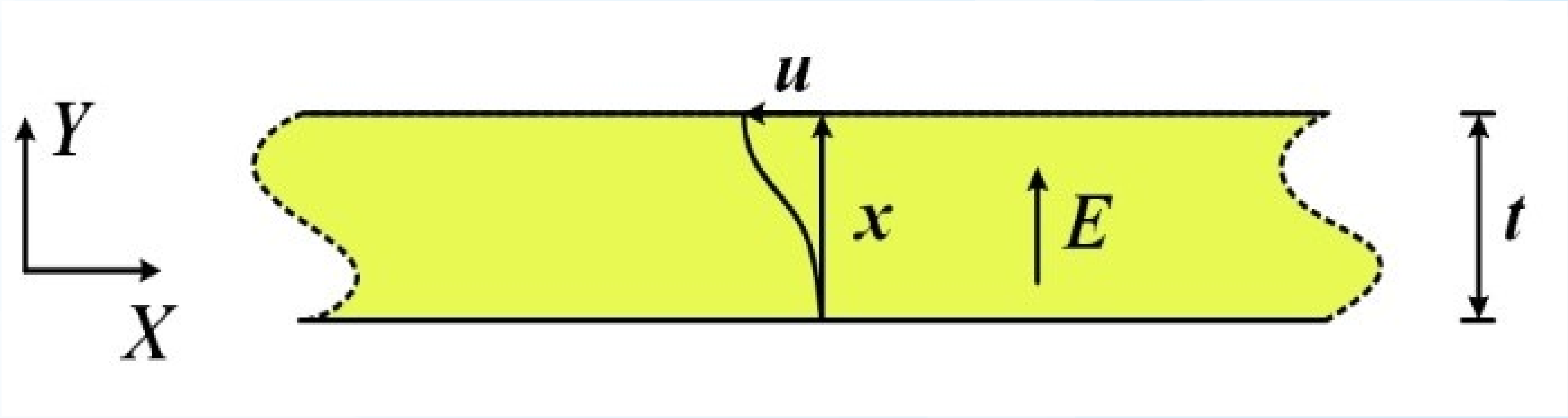
3D piezoelectric equations

$$\begin{pmatrix} c & e^T \\ e & \varepsilon \end{pmatrix} \cdot \begin{pmatrix} S \\ E \end{pmatrix} = \begin{pmatrix} T \\ D \end{pmatrix}$$

$$\begin{pmatrix} s & d^T \\ d & \varepsilon \end{pmatrix} \cdot \begin{pmatrix} T \\ E \end{pmatrix} = \begin{pmatrix} S \\ D \end{pmatrix}$$

$$s = c^{-1}$$

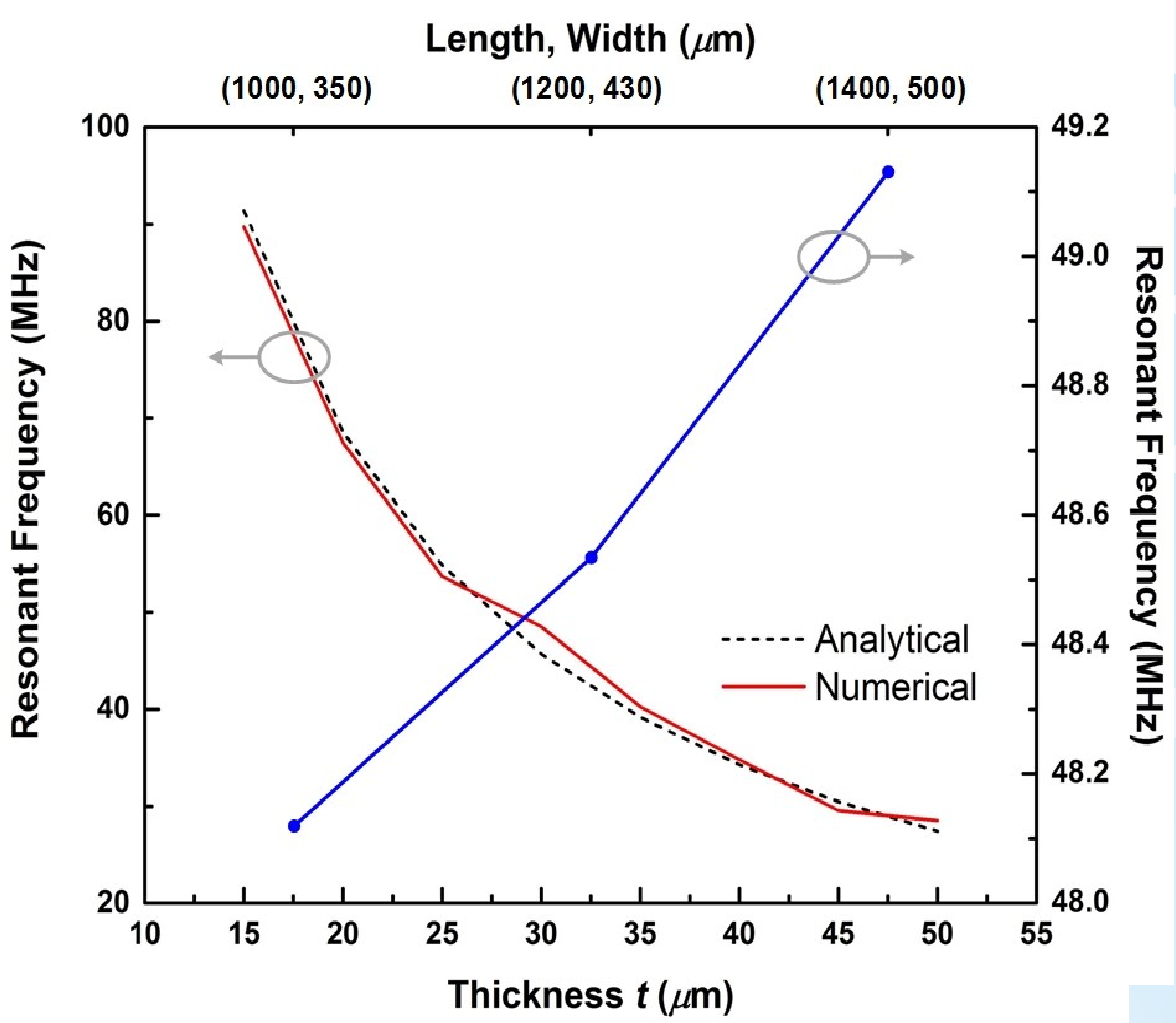
$$d = e \cdot s = e \cdot c^{-1}$$



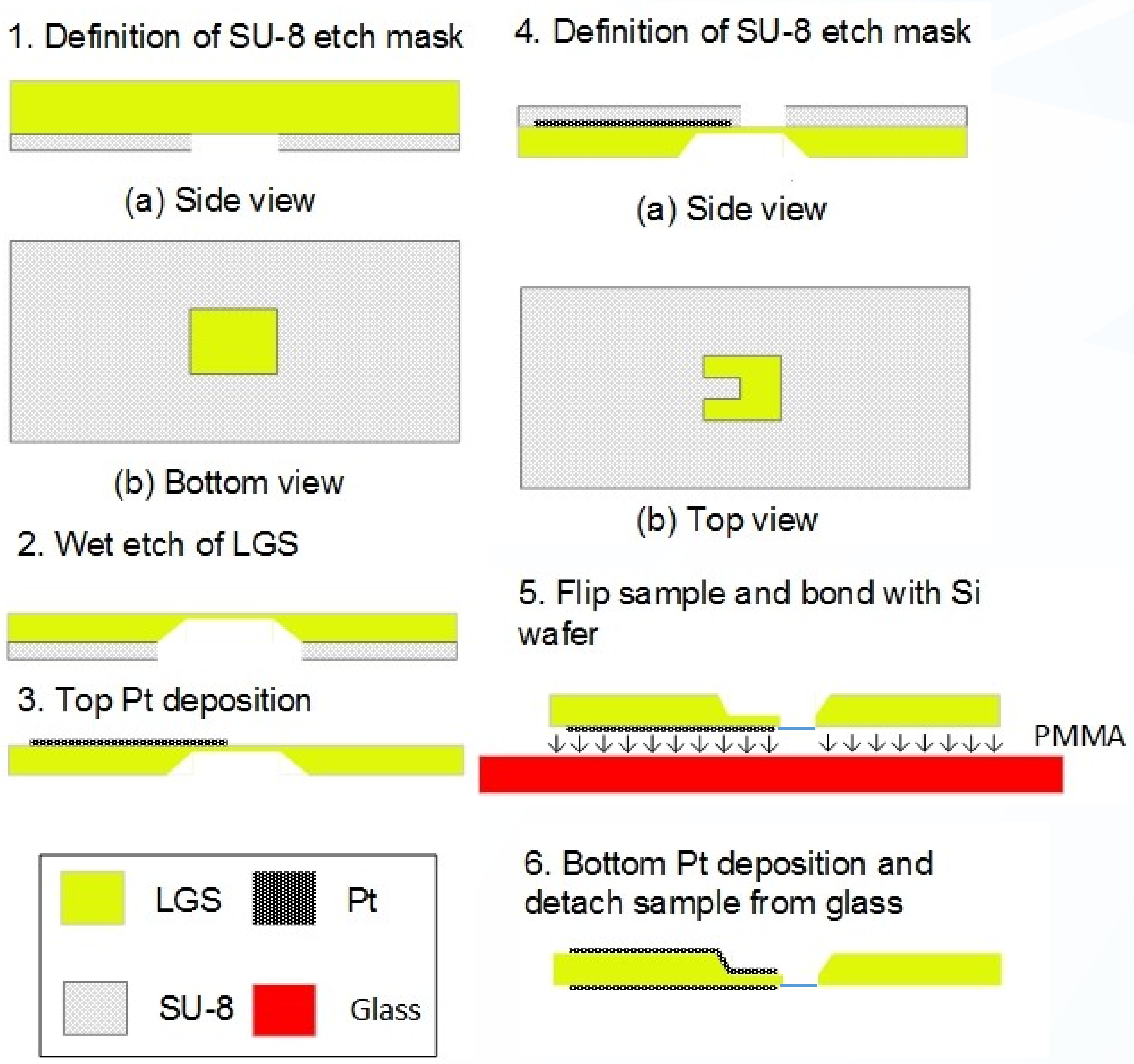
Thickness shear mode vibration of LGS MEMS

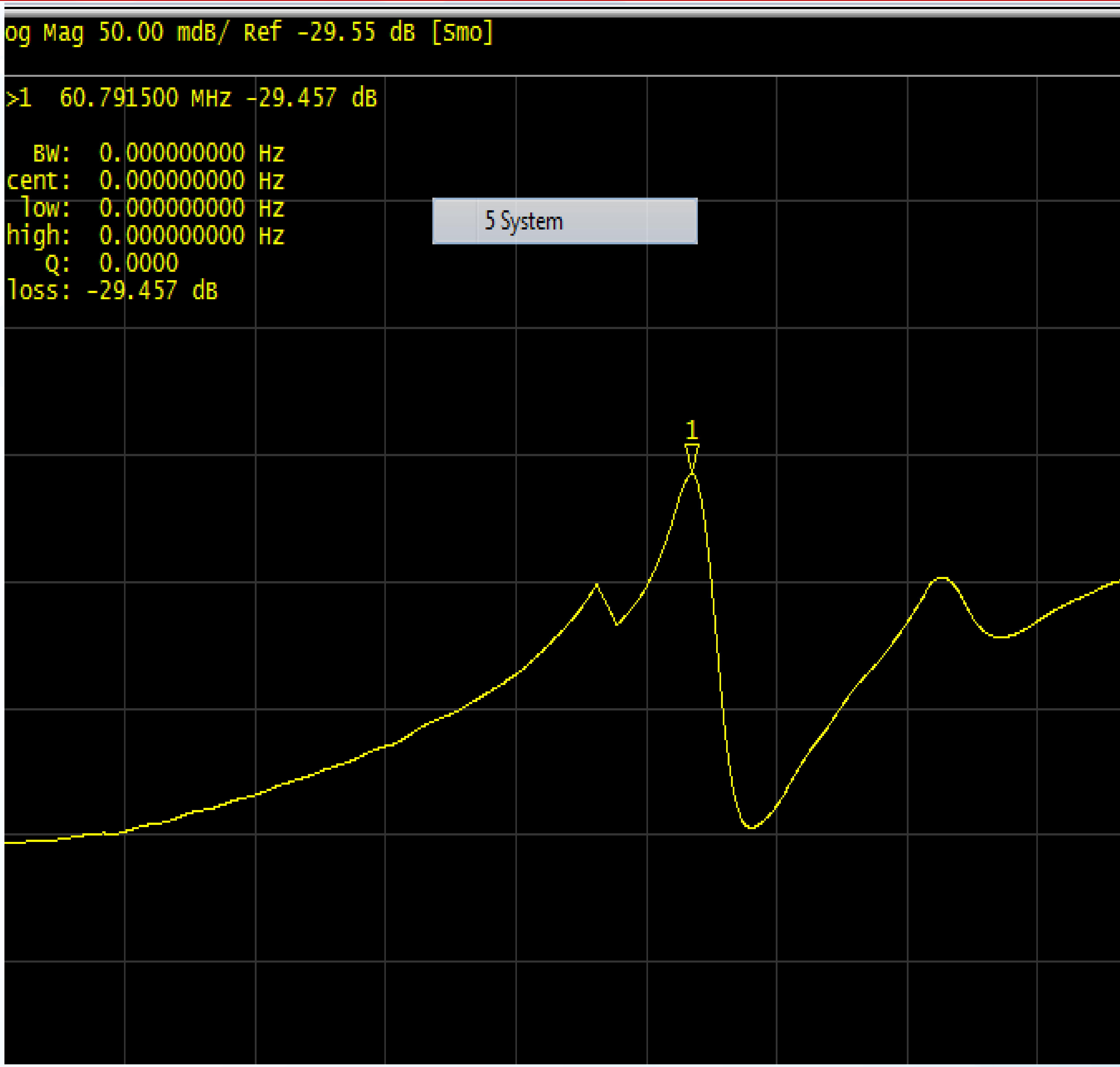
The resonant frequency of thickness shear mode resonance is **uniquely determined** by the **material properties** as well as the cantilever **thickness** ***t*** instead of its structured length and width.

- **Thickness of the resonator determines its resonant frequency**
- **Analytical results match the numerical results**
- **Length/width also affects the resonant frequency with a negligible effect.**



LGS MEMS fabrication





LGS MEMS with ZnO thin film for gas sensing

$$O_2 \rightarrow O_2(ads) \quad \Rightarrow \quad O_2(ads) \rightarrow O^- \quad \Rightarrow \quad CO_2 + O^- \rightarrow CO_3^{2-}$$

Sample exposed to gas species with certain concentration

Chemical reaction with electron transfer take place at the solid-gas interface

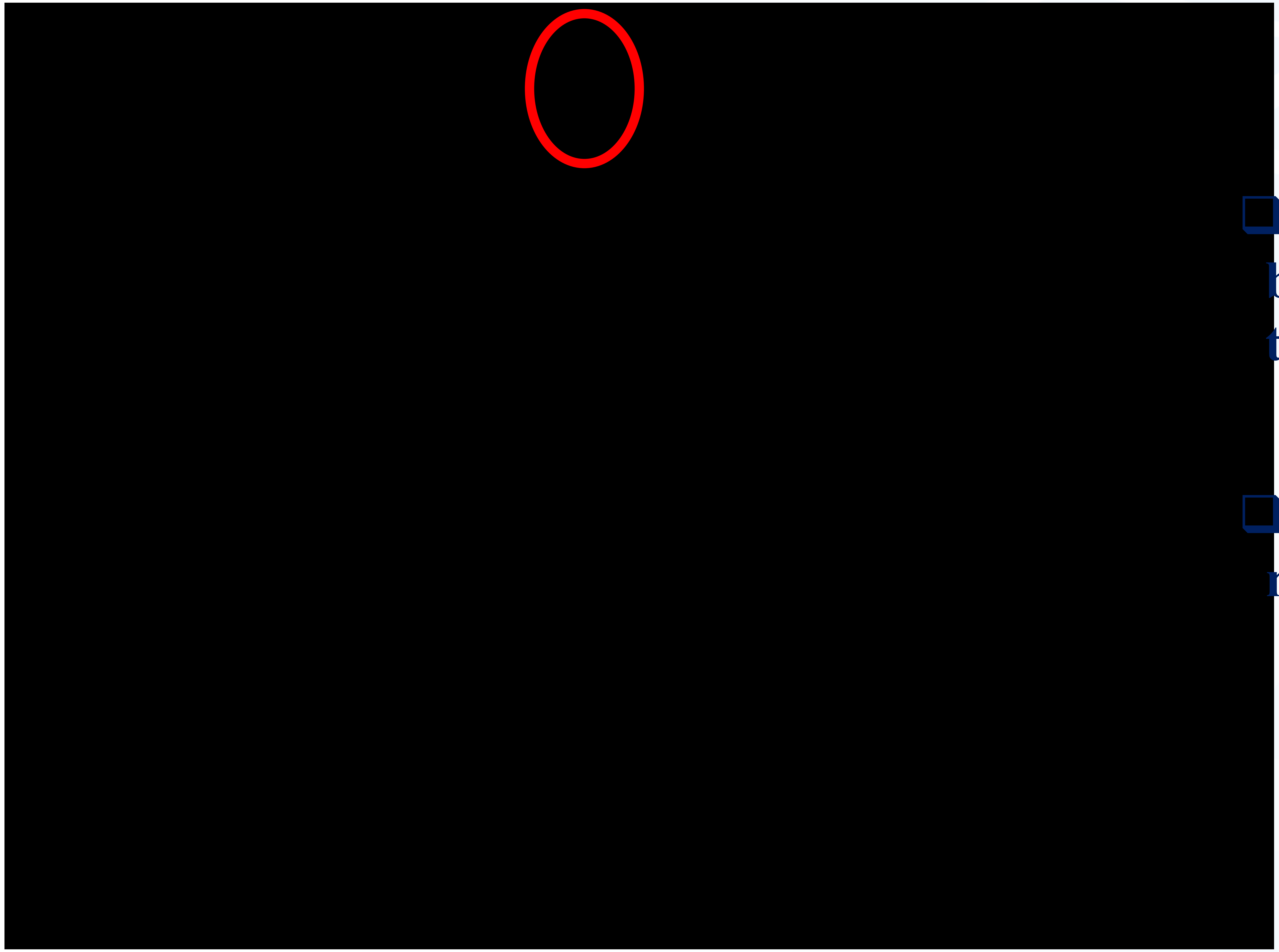
Gas molecules are chemisorbed on the resonator surface

Frequency drift induced by added mass from chemisorption

Temperature change

Gas concentration change

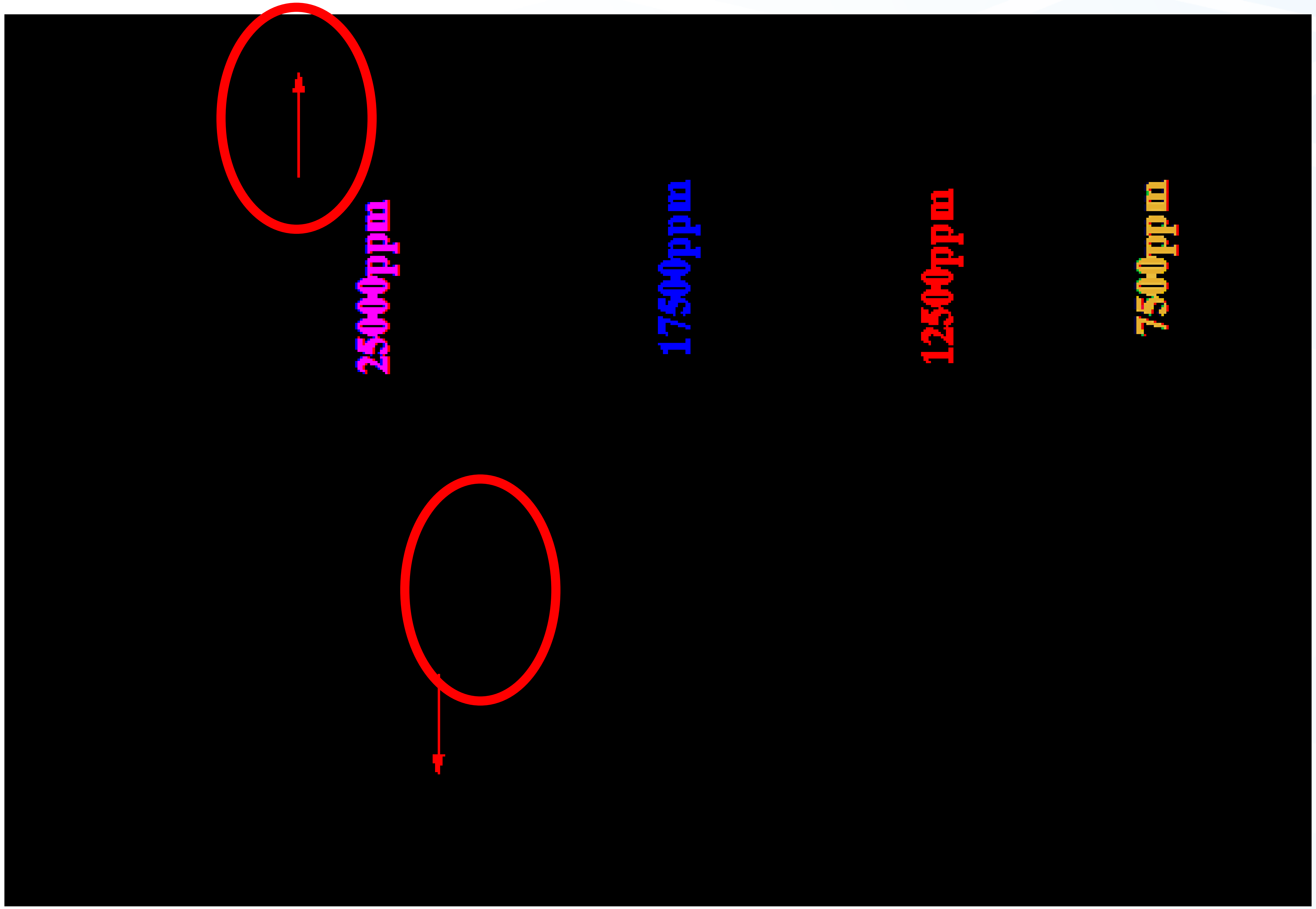
LGS MEMS with ZnO thin film for gas sensing



- Sensor is tested with 100% pure CO_2, by which the resonant frequency drift of the sensor is tracked.

- Optimum temperature is 400^{o}C, where maximum sensor response is measured.

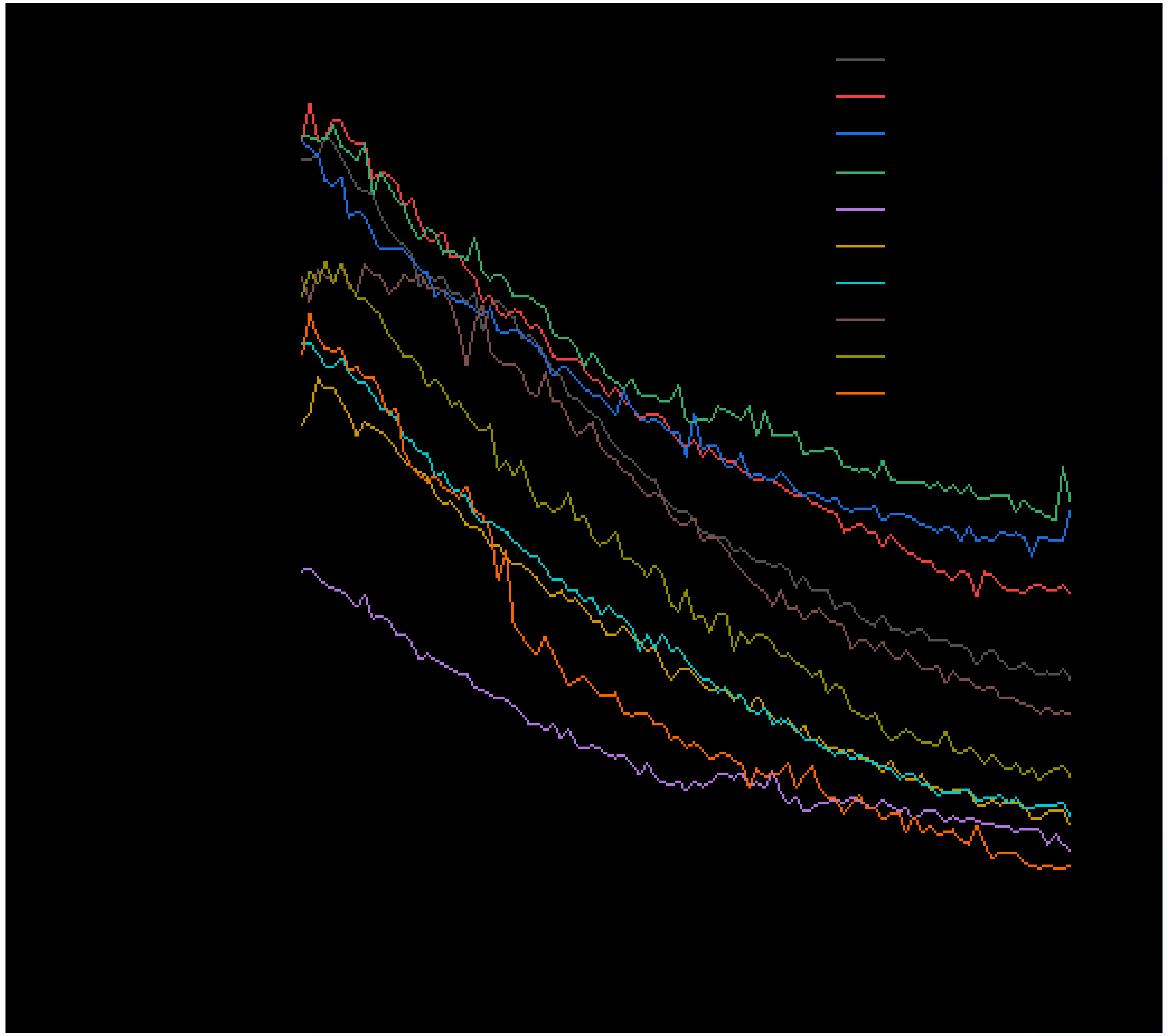
LGS MEMS with ZnO thin film for gas sensing



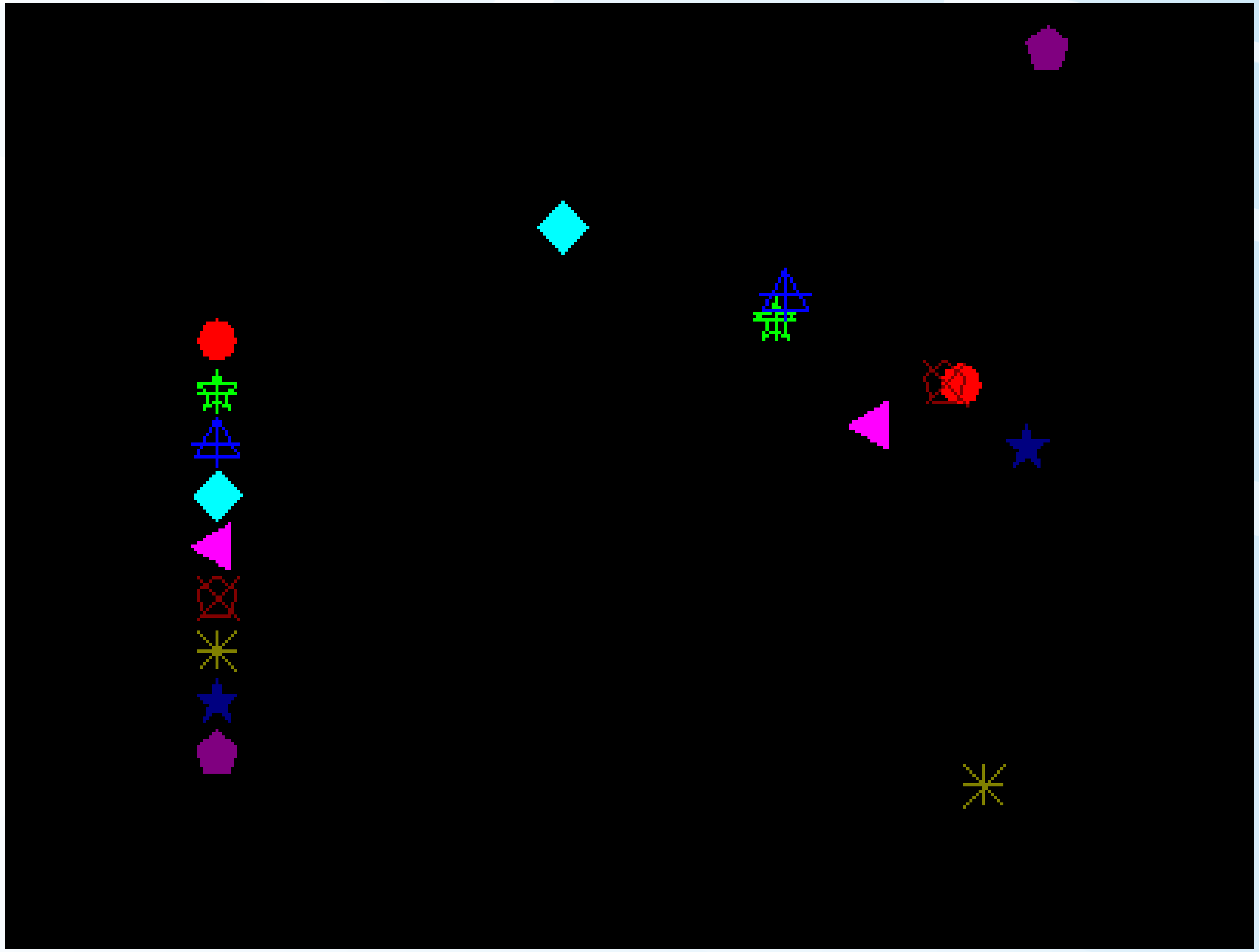
Resonators	Maximum Relative Sensitivity (df/f0/delta ppm)
LGS MEMS micro-cantilever with ZnO	0.02
Naked QCM	6.67e-6
QCM with calix [2] modified CNT films	1.25e-5
QCM with rough Ag electrode	8e-5
Unpolished QCM with PMMA film	1.2e-4
QCM with Multivalent Amino-Functionalized calix[4]arenes	2e-4
Multilayered ZnO FBAR gas sensor	1.18e-3

LGS MEMS with ZnO thin film for gas sensing

Cross-sensitivity is analyzed for real environment gas sensing application with the principle component analysis (PCA) technique.



ZnO thin film based LGS MEMS micro-cantilever gas sensor PCA results: PC2 vs. PC1 plot for N_2, air, and 100% CO_2 at 400°C.



Conclusion and Future works

Conclusion

- ❑Piezoelectric-based BAW resonator (MEMS micro-cantilever) are responsive to mass loading from various test gas concentration/species. Their sensitivities are dependent on the nature of the material, vibration mode, and sensing thin film deposition.
- ❑MEMS resonator can be successfully applied for potential gas sensing and performs an outstanding sensitivity by taking the advantage of their high resonant frequency as well as utilization of sensing thin films
- ❑Metal oxides (ZnO) can improve the sensing performance by acting as catalyst for oxygen pre-adsorption at certain temperature as well as the chemisorption of test gas species.

Future works

- ❑Performance enhanced MEMS technique will be adopted, which is expected to improve the Q-factor of MEMS micro-cantilever resonator.
- ❑Real environment tests will be carried out with performance enhanced gas sensor for a comprehensive mixed gas measurement, which is expected to address the gas sensing problem in reality.
- ❑Sensor pack or sensor fusion will be implemented to exploit a gas sensing terminal with advanced sensor signal processing algorithm for future commercial/industrial application.

Acknowledgments

Mr. Zhang Chen, Dr. Abihesh Ghosh, Dr. Suresh Kaluvan, Mr. Pham Toug

USDA

NSF

UNT UNIVERSITY OF NORTH TEXAS

Questions