CO_2 GAS SENSOR BASED ON MIS STRUCTURE WITH A LAYER OF F^--CONDUCTING MATERIAL LaF_3

I.R.Shandova[1], A.V.Varfolomeev[1], A.A.Vasiliev[1,2], A.S.Lagutin[1], W.Moritz[3]

[1]RRC Kurchatov Institute, Institute of Applied Chemical Physics, Moscow, Russia
[2]OJSC "RTI", Moscow, Russia
[3]Humboldt University of Berlin, Institute of Chemistry, Berlin, Germany
vasiliev@iacph.kiae.ru

Motivation

The aim of this research is to find a CO_2-sensor with sufficiently high response to CO_2 concentrations in a range of some hundreds ppm, with short response and recovery time, working at room temperature, which could be applied, for example, in air conditioning.

Detection possibilities

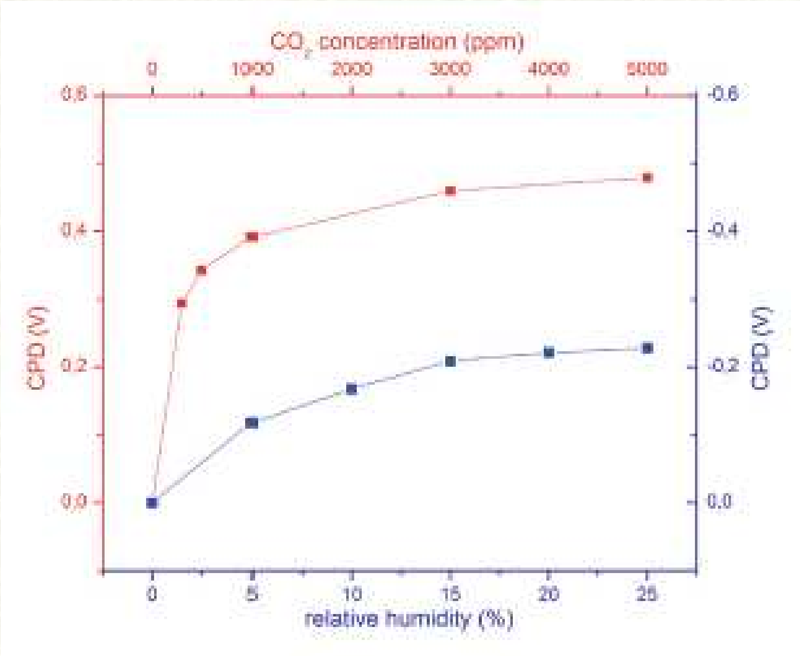
- ***IR NDIR gas sensors based on thermal and LED IR radiation sources***
- ***Resistive type gas sensors based on LaO(OH) sensing material (University of Tuebingen)***
- ***Suspended gate transistor measurements (Siemens AG)***
- ***Work function measurements with ZnO/Al sensing layer (Siemens AG)***
- ***MIS structures with solid electrolyte layer***

NDIR detection of CO_2

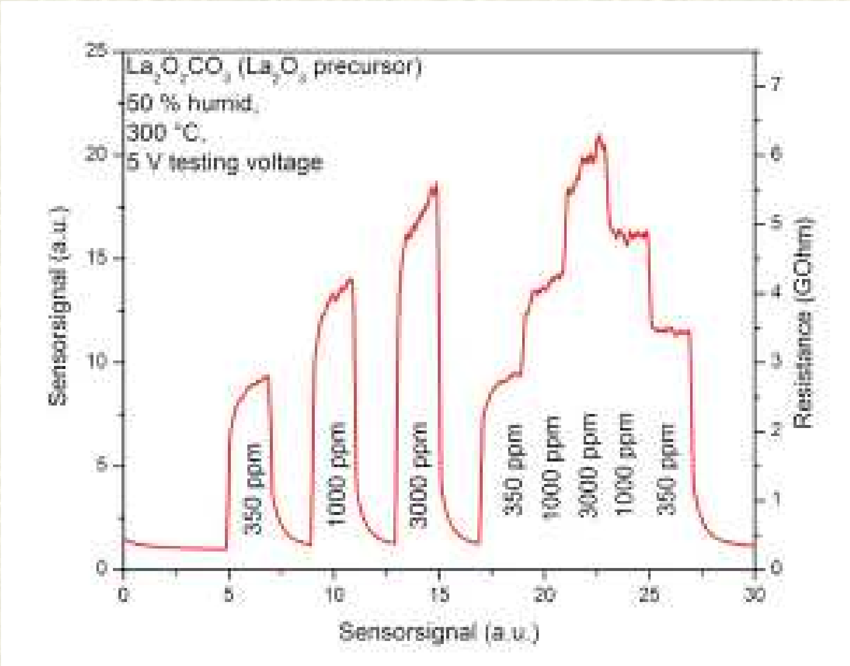
NDIR CO_2 sensor based on LED (4.2 μ). OptoSense company (St-Petersburg, Russia)

Low cost sensor module of Korean company ELT (thermal source)

Resistive type CO_2 sensor based on LaO(OH).



CPD differences for various concentrations of CO_2 (N.Barsan et al., Eurosensors-2011)

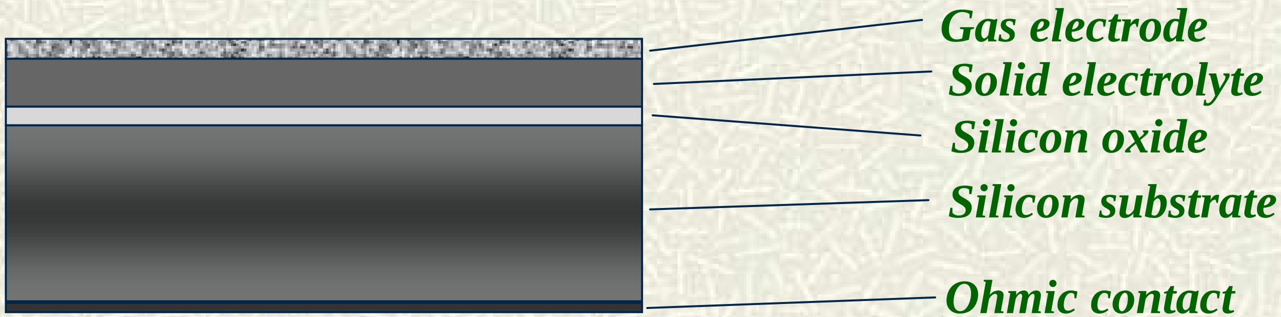


Response of the sensor based on LaO(OH) to CO_2 concentration. x-axis – in hours.

Work-function measurements with ZnO/Al sensing material

Recent results presented at the Eurosensors-2013 conference show the prospective of work function measurements of CO_2 response of ZnO/Al sensing material.

Operation of the sensor based on MIS structure with solid electrolyte layer

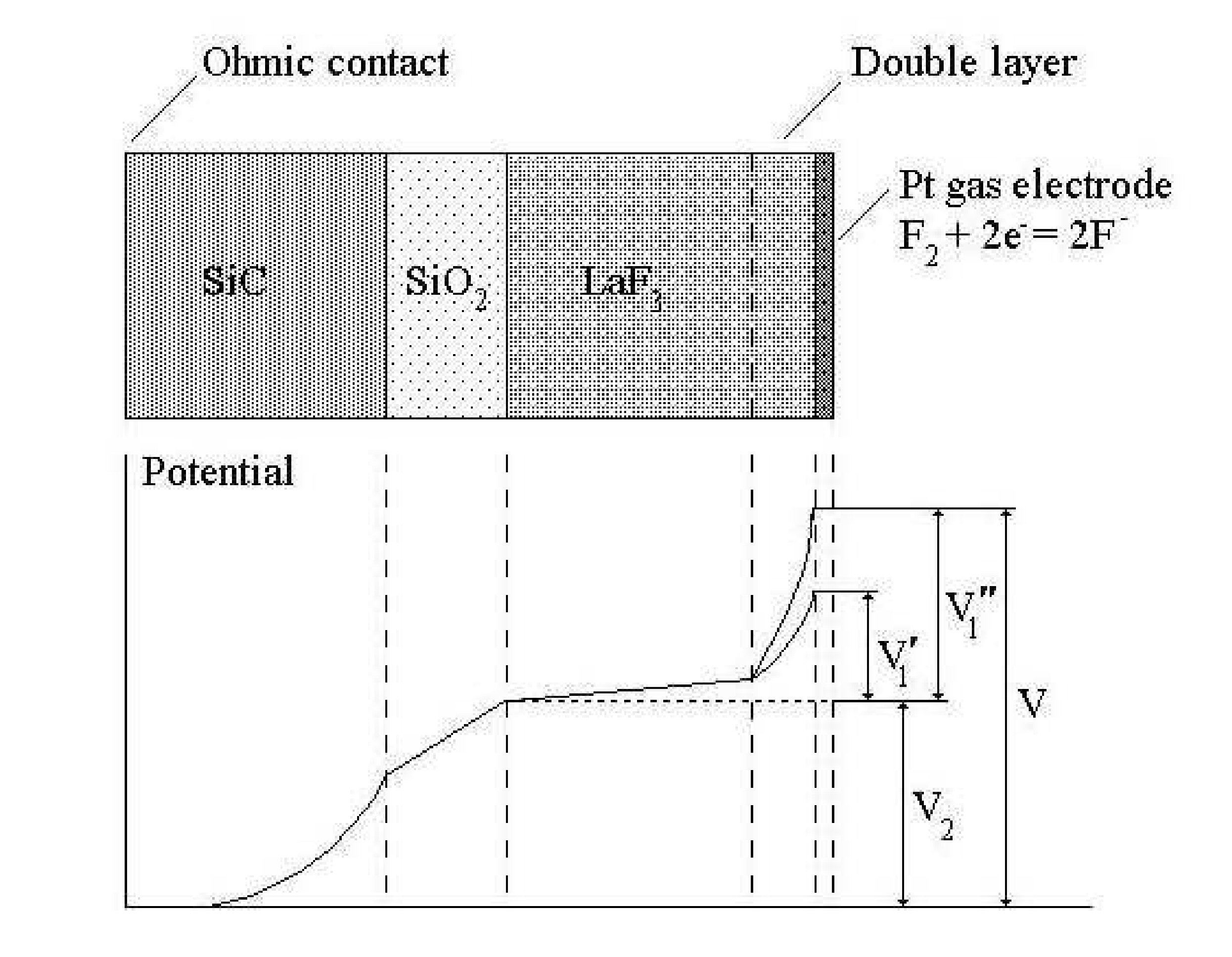


$$X + ne^{-} \Leftrightarrow X^{n-}$$

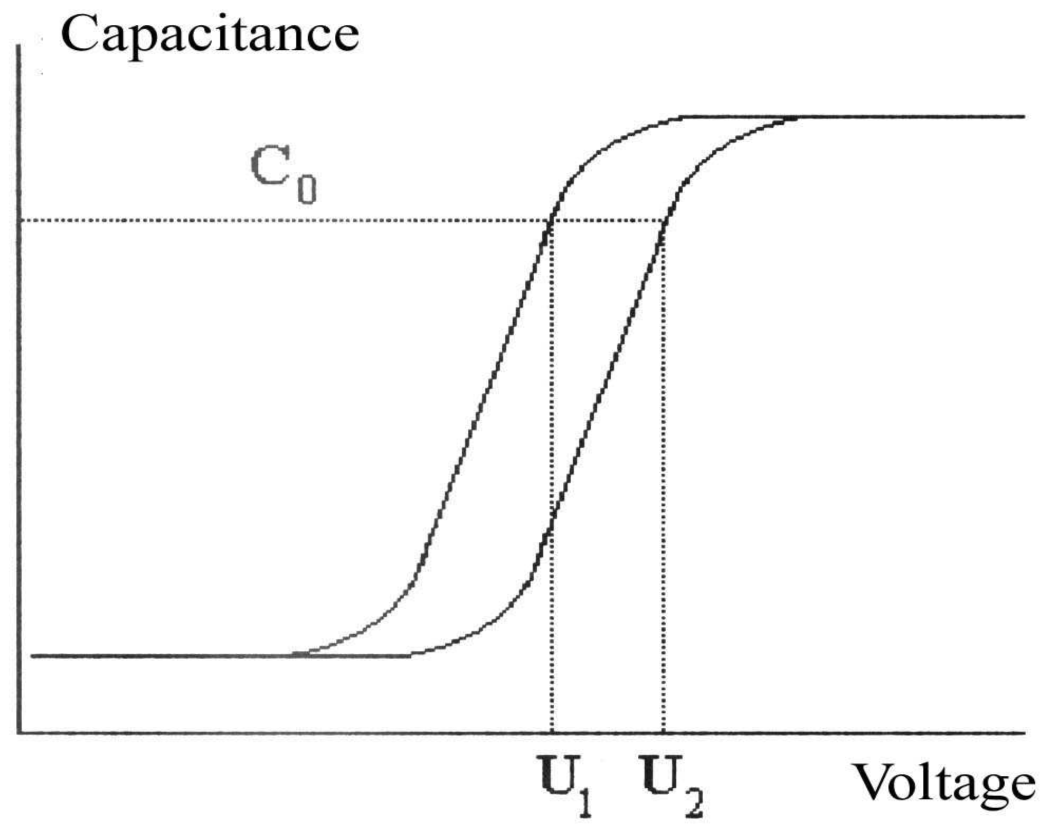
$$E = E_0 + \frac{RT}{nF}\ln(P_x)$$

$$\Delta E = 2{,}303\frac{RT}{nF}(\log(P_2) - \log(P_1)) = 2{,}303\frac{RT}{nF}\log(\frac{P_2}{P_1})$$

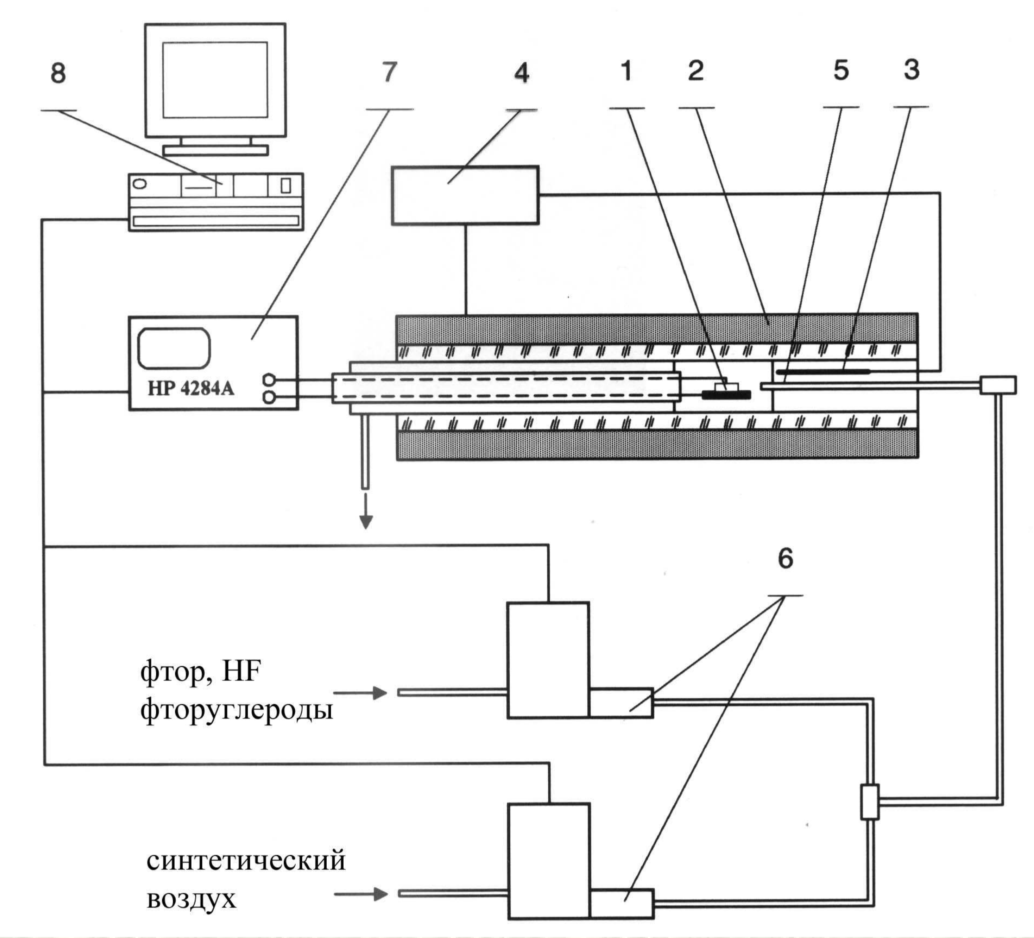
Distribution of potential in the structure metal/solid electrolyte/semiconductor



Shift of CV-characteristics of the structure metal/solid electrolyte/semiconductor

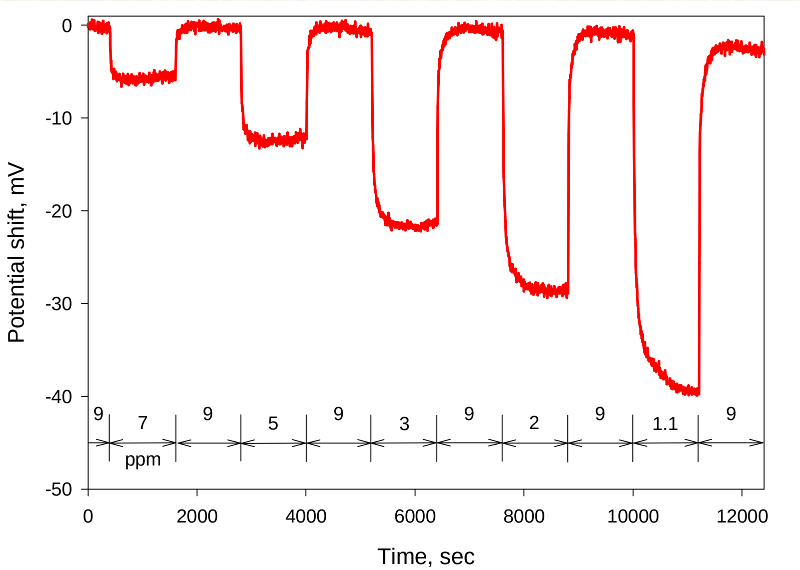


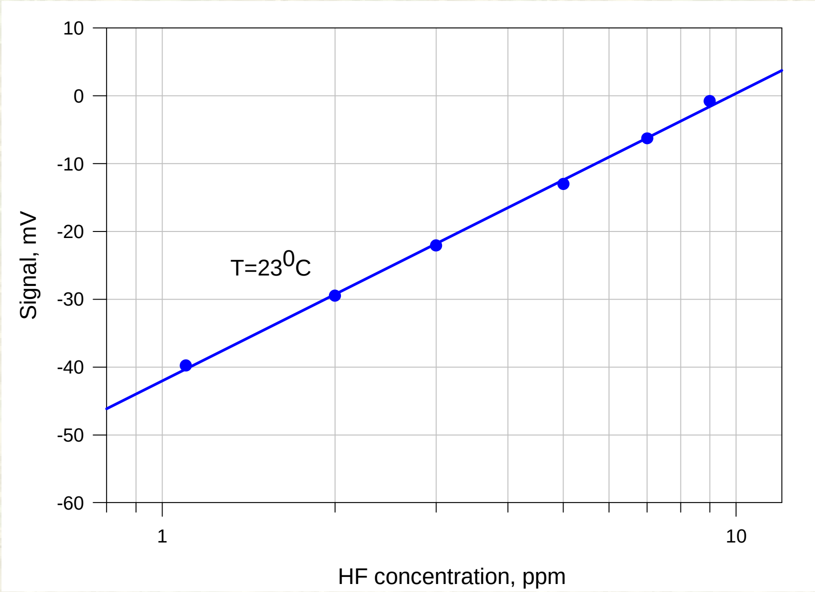
Scheme of the installation for the measurement of sensitivity of gas sensors



1 – measurement cell,
2 – heater,
3 – Pt/Pt-Ph thermocouple,
4 – controller of the heater,
5 – capillary tube,
6 –mass-flow controllers,
7 – RCL-meter,
8 – IBM PC.

Response of MEIS structure with LaF_3 solid electrolyte layer to HF

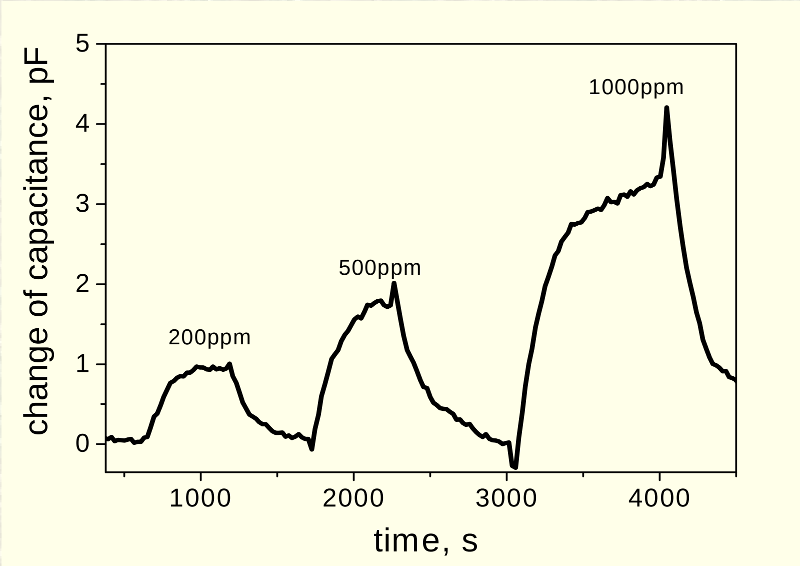


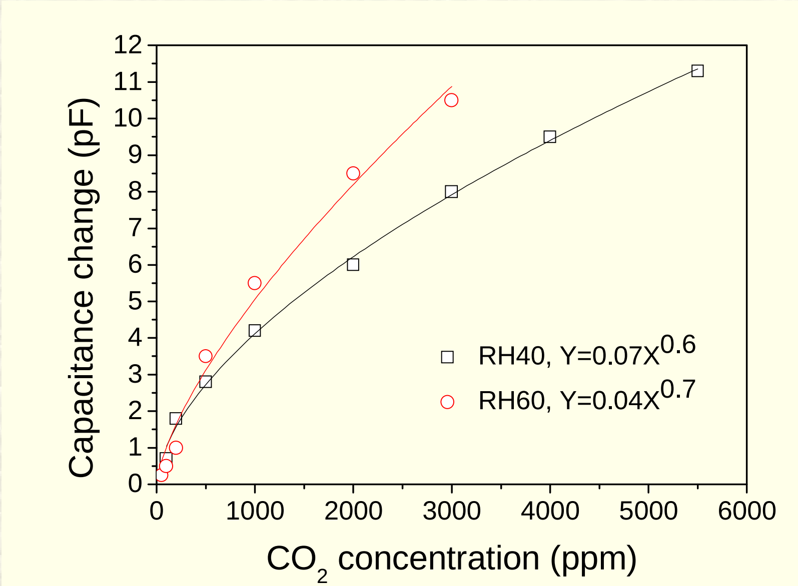


HF response of the structure $Pt/LaF_3/SiO_2/SiC$ at room temperature

HF sensitivity is 45±3 mV/dec.

MIS (MEIS) structure gas sensor with a layer of proton conducting solid electrolyte (PVA/PSA)





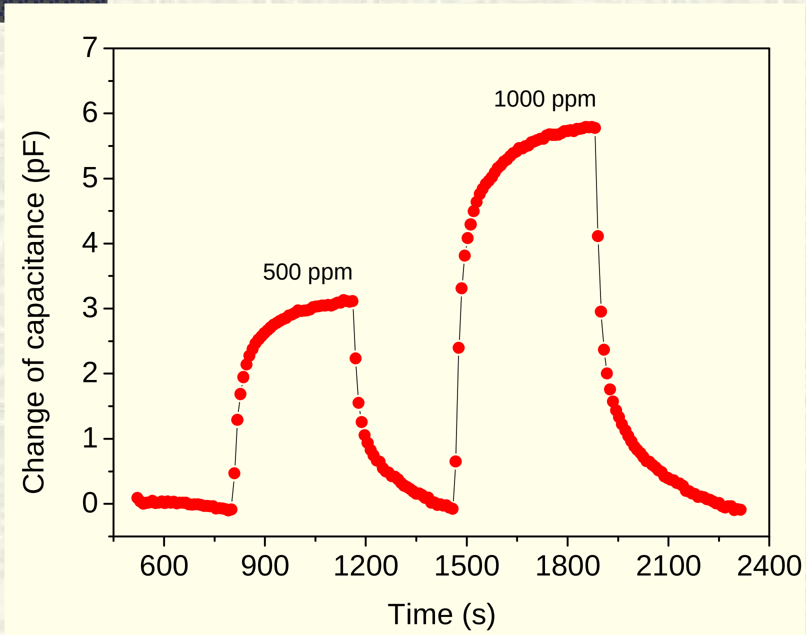
Response of the MEIS structure to different concentrations of CO_2 in air at RH80

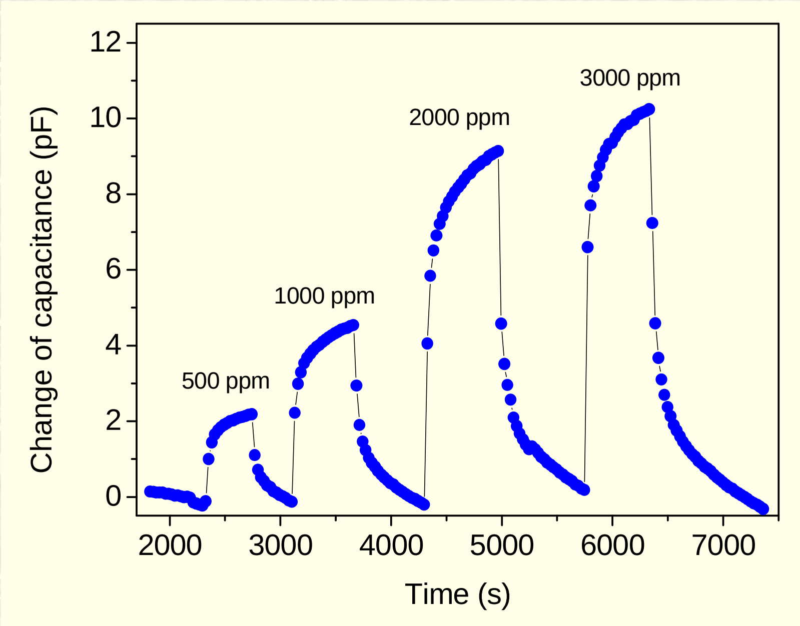
Response of the MEIS structure to different concentrations of CO_2 in air at RH40 and RH60

Why LaF_3 is a promising candidate for CO_2 sensing layer?

- *$La_2(CO_3)_2$ has low decomposition temperature (< 400^0C).*
- *Fluorocarbonate can be decomposed at temperature < 200^0C.*
- *Activation procedure of the MEIS sensor used for the detection of O_2 and H_2 leads to the desorption of CO_2 (mass-spectrometry).*
- *Activation procedure can be very sharp, time ~ 10 ms is sufficient.*

Response of MEIS structure with a layer of LaF_3 to CO_2 concentrations

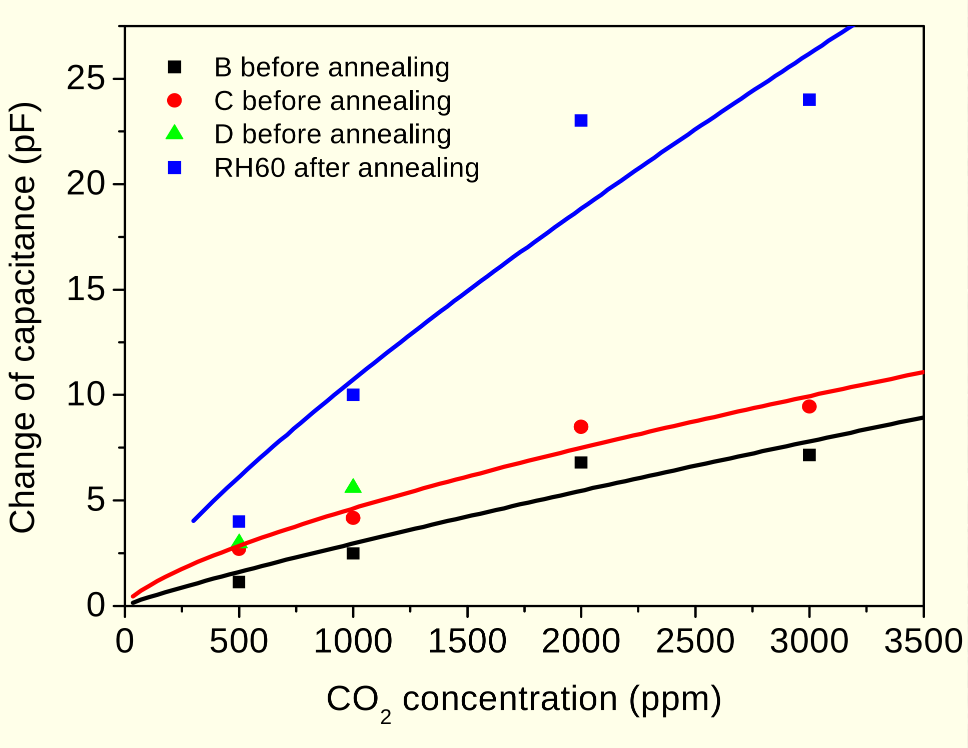




Responses to different CO_2 concentrations at constant relative humidity equal to 80 % before sensor activation.

Responses to different CO_2 concentrations at constant humidity equal to 60 % before sensor activation.

Sensitivity of MEIS sensor to CO_2 concentrations



Change of capacitance as a function of CO_2 concentration and fits according to a power law $y=ax^b$ (solid lines). Black, red, and green dots – the measurements were performed with sensor without activation (heating at 300^0C for 10 min). Blue dots – sensor after activation.

Conclusions

- *MIS structure with a layer of fluorine conductive solid electrolyte LaF_3 is sensitive to CO_2 in air. This sensitivity is due to the formation of $La(OH)F_2$ on the surface of LaF_3 layer followed by reversible chemisorption of CO_2.*
- *Sensor response increases after the "activation" procedure. This activation consists in heating the sensor on air up to 300^0C during approximately 1 min. Sensor activation leads to the desorption of CO_2 from the surface of fluorine conductive layer.*
- *The sensor is free of disadvantages found for the sensors of resistive type, which have very high resistance inconvenient for practical application of the device. Detection limit of the MIS structure is of about 100 ppm, this value is below the background concentration of clean atmospheric air (~300 ppm).*