European Network on New Sensing Technologies for Air Pollution Control and Environmental Sustainability - *EuNetAir*

COST Action TD1105

WGs & MC Meeting at SOFIA (BG), 16-18 December 2015

New Sensing Technologies for Indoor Air Quality Monitoring: Trends and Challenges

Action Start date: 01/07/2012 - Action End date: 30/04/2016 - Year 4: 1 July 2015 - 30 April 2016

FLUORINE CONDUCTIVE POLYMER COMPOSITE FILMS FOR GAS SENSING APPLICATION

Alexey Vasiliev

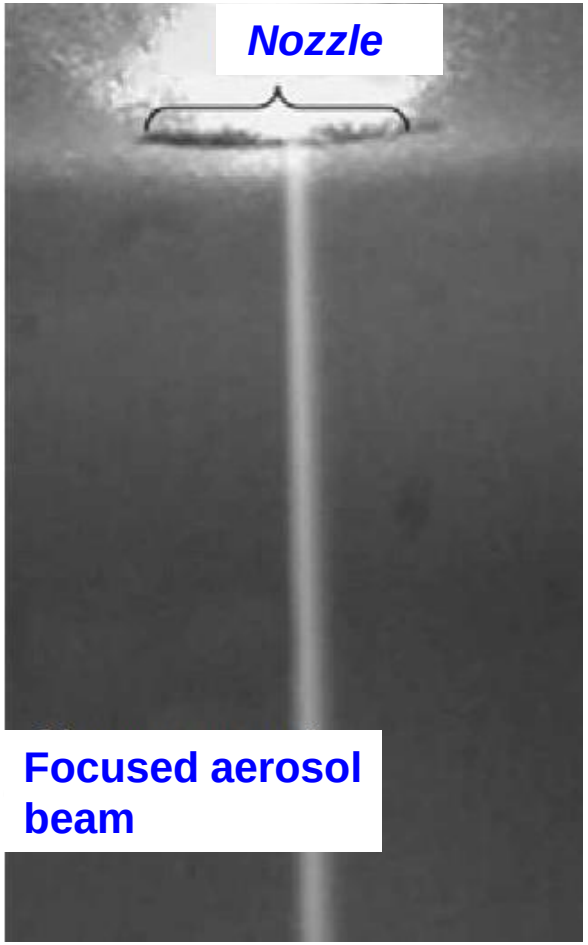
National research center "Kurchatov Institute", Moscow, Russia

Email: A-A-Vasiliev@yandex.ru

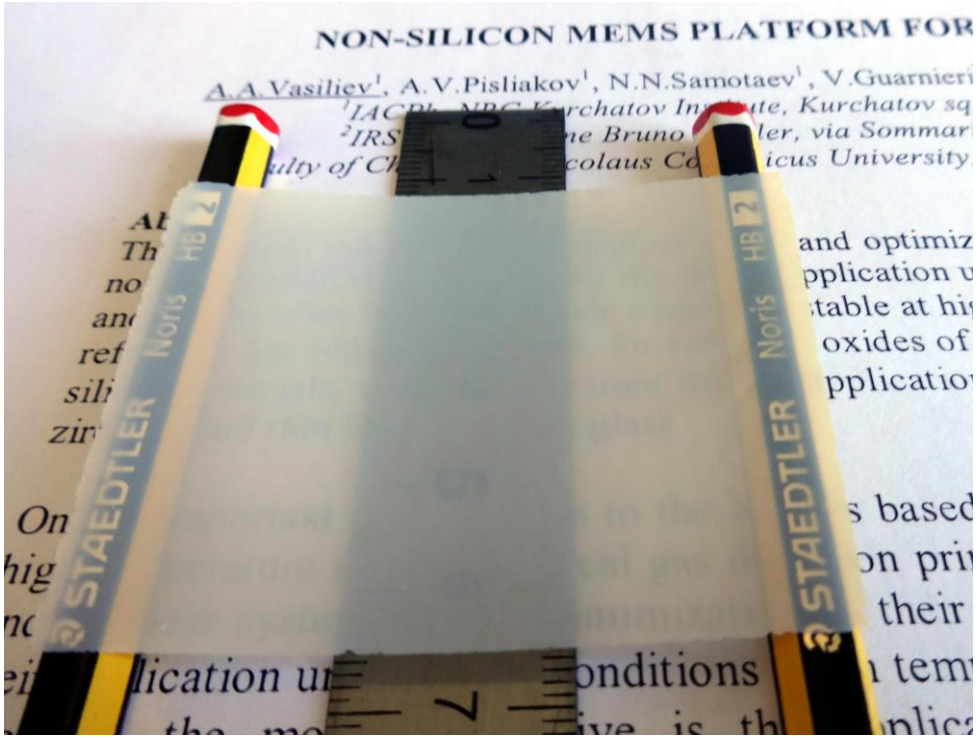
COST is supported by the EU Framework Programme

ESF provides the COST Office through a European Commission contract

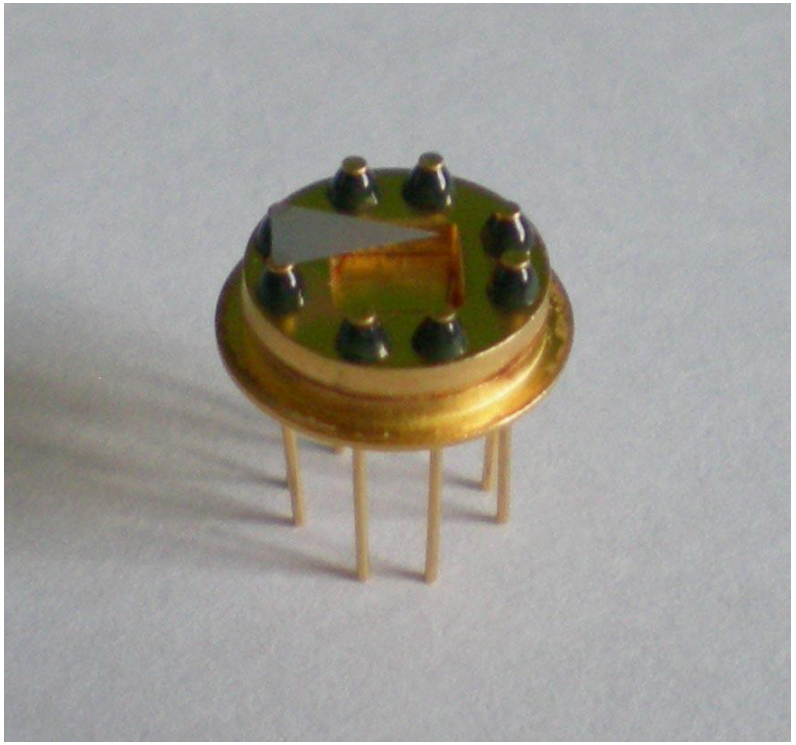
Aerosol printing machine



Substrates Made by Anodic Oxidation of Aluminum Foil

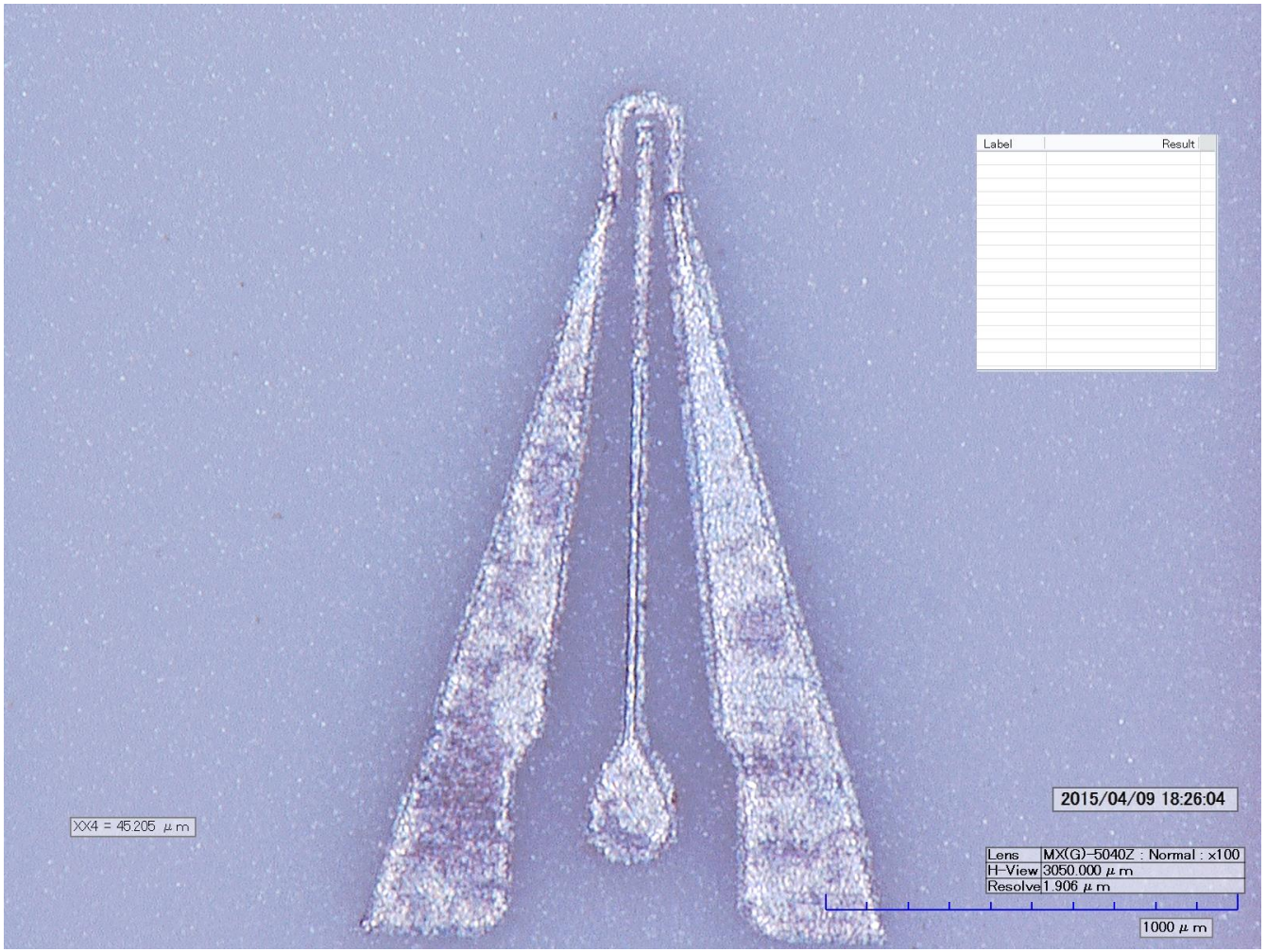


Alumina film (12 μm thick) prepared by anodic oxidation of aluminium followed by annealing at 800⁰C. Membrane size is of 48x60 mm.



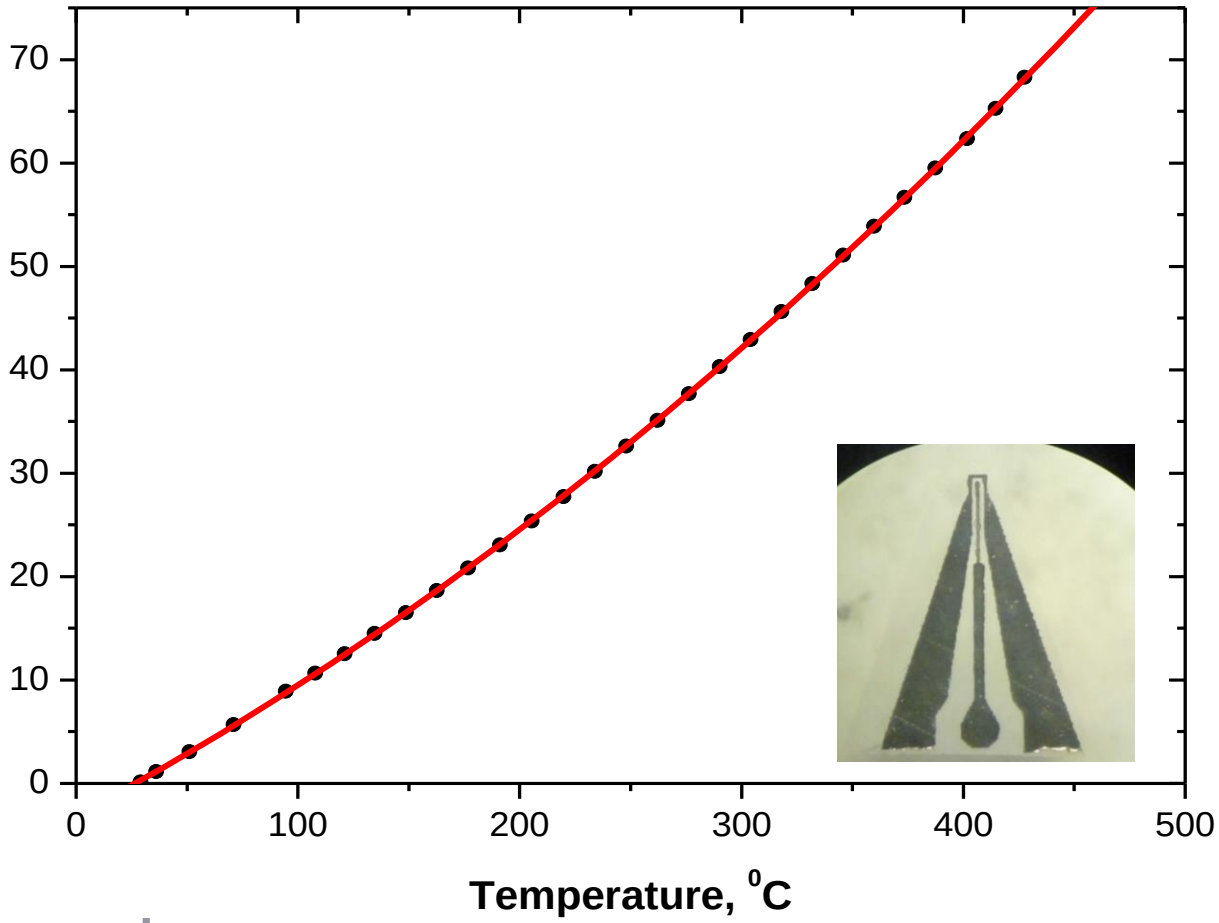
Alumina cantilever chip in TO8 package. Alumina film thickness is of 12 μm.

Cantilever Sensor Layout Obtained Using Aerosol Jet Printer

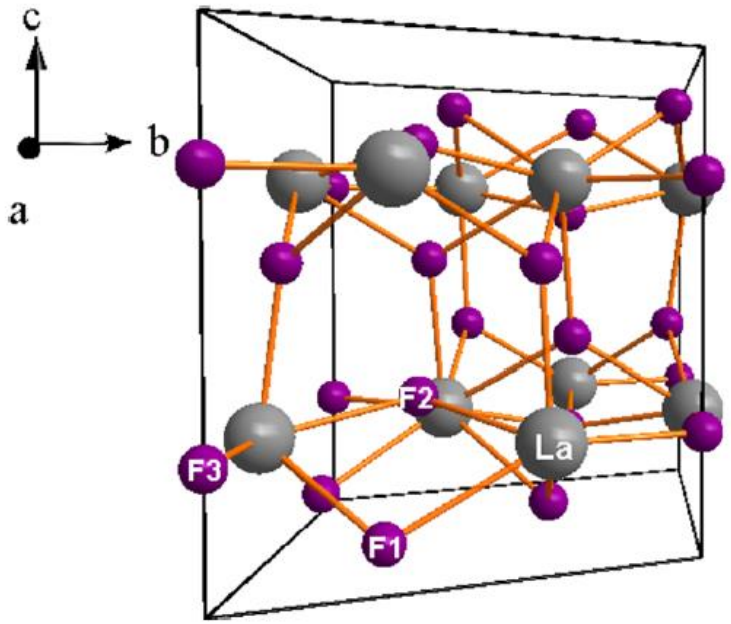


Printing with Pt based ink of alumina substrate. Line width and gaps are of about 40 μm.

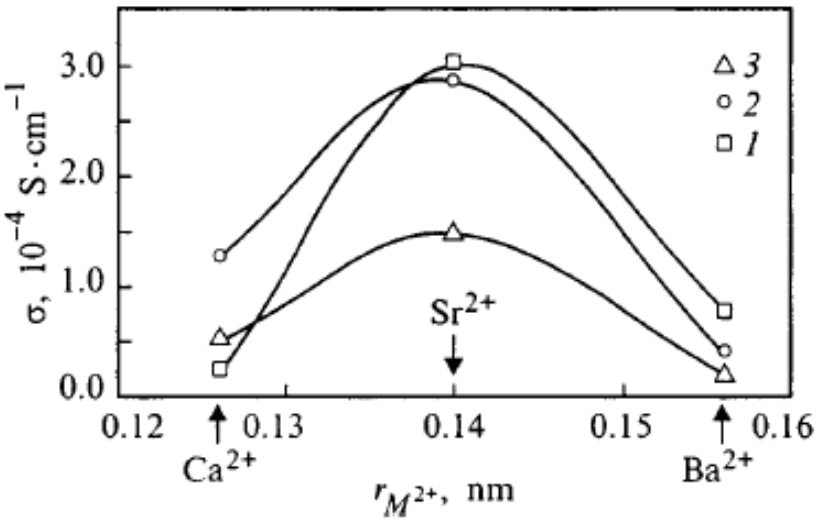
Power consumption of printed microheater as a function of temperature



Rare earth trifluorides as fluoride ion conducting materials



Tysonite type structure of LaF_3



Variation of the conductivity of the conductivity of (1) $La_{0.95}M_{0.05}F_{2.95}$; (2) $Pr_{0.95}M_{0.05}F_{2.95}$; (3) $Nd_{0.95}M_{0.05}F_{2.95}$ as a function of ionic radius of doping element M.

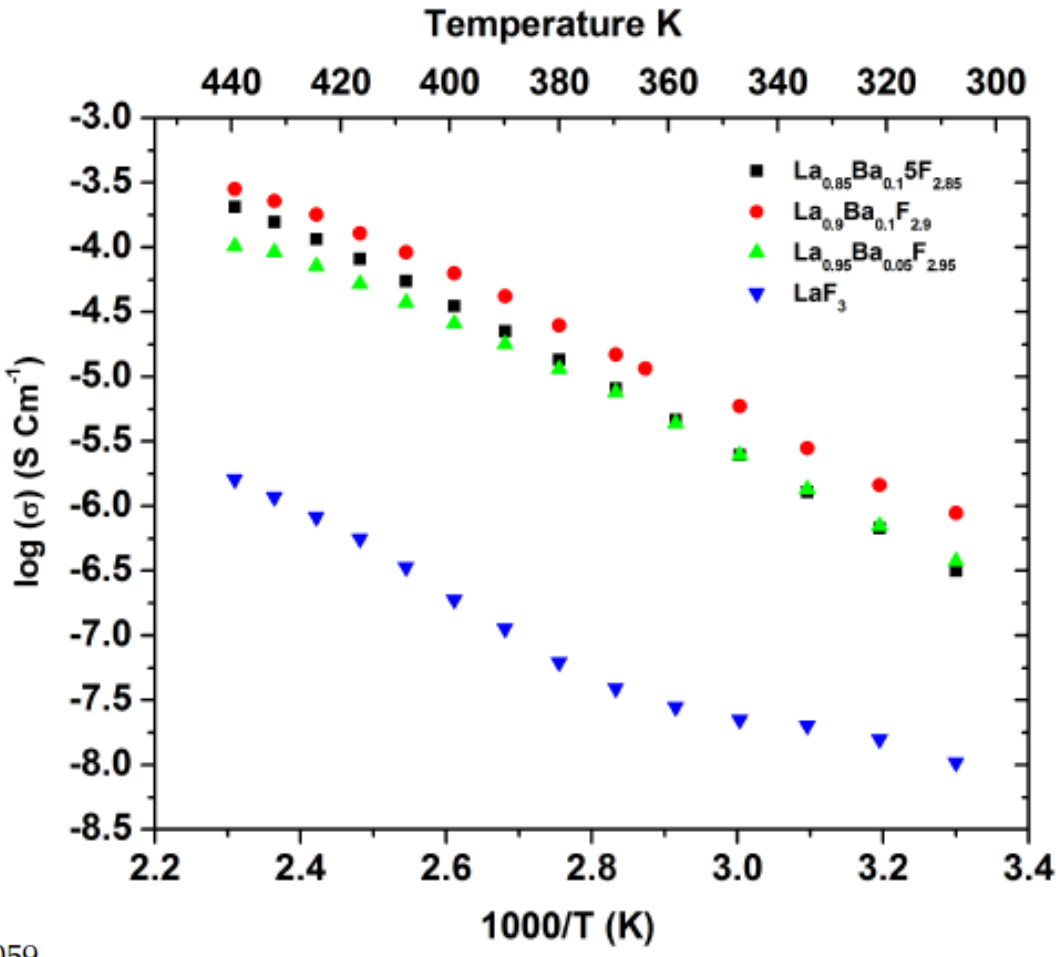
N.I. Sorokin, E.A. Krivandina, Z.I. Zhmurova, B.P. Sobolev, M. V. Fominykh and V.V. Fistul, *Phys. Solid State* 41 (1999) 573.

Target

The target of the work is the study of the possibility to fabricate fluorine ion conducting films using printing technology. The application of such films could be gas sensors, fluoride rechargeable batteries, ion selective electrodes.

Ionic conductivity of doped lanthanum trifluoride as a function of temperature

Arrhenius plot for the ionic conductivity of nanocrystalline $La_{1-x}Ba_xF_{3-x}$ (0<x<0.15)



M. Anji Reddy and M. Fichtner, *J. Mater. Chem.* **21** (2011) 17059.

Methods of solid electrolyte preparation

- ***Synthesis of single crystals of doped LaF_3.***
- ***Laser melting of mixture of LaF_3/BaF_2 (SrF_2) powder mixture.***
- ***High-temperature isostatic pressing of LaF_3/BaF_2 mixture.***
- ***Thermal evaporation of LaF_3 in high vacuum conditions.***

Problem – high melting temperature of LaF_3 (1493°C).

Sensor operation

At low F_2 concentrations in potentiometric mode

$$F_2 + 2e^- \Leftrightarrow 2F^-$$

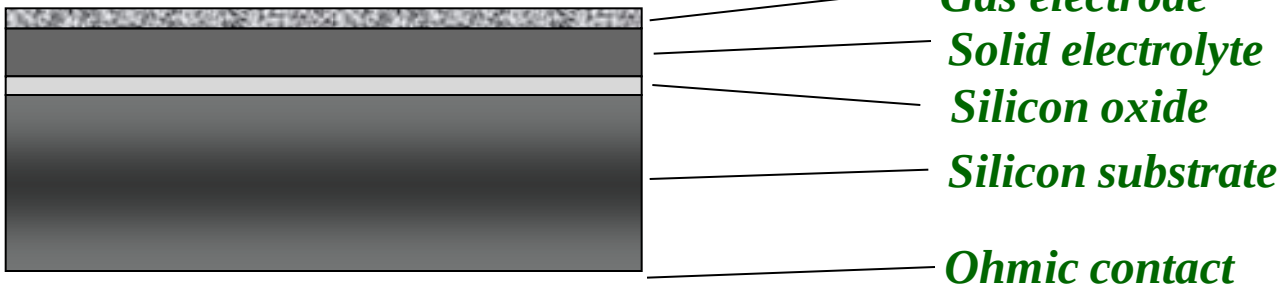
$$\Delta E = 2{,}303 \cdot \frac{RT}{nF} \log\left(\frac{C_2(F_2)}{C_1(F_2)}\right) = 29 \cdot \log\left(\frac{C_2(F_2)}{C_1(F_2)}\right)$$

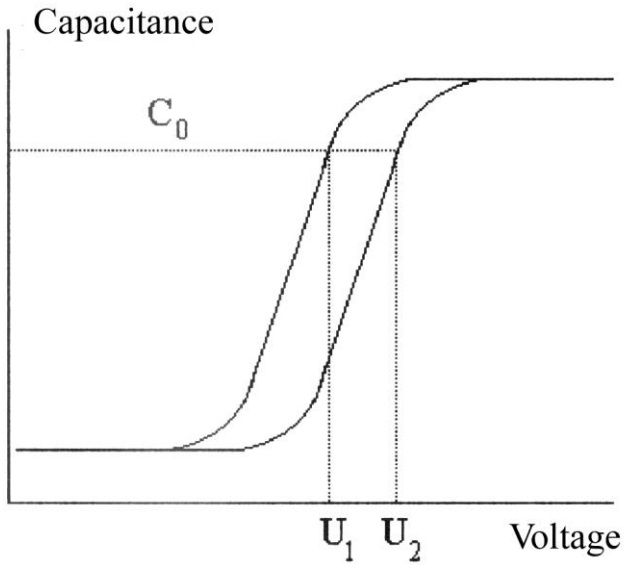
This mode works, for example, in MIS structure sensors with solid electrolyte layer.

In pure electrochemical sensors amperometric mode is more suitable. Diffusion through platinum layer is a limiting step (bottle neck).

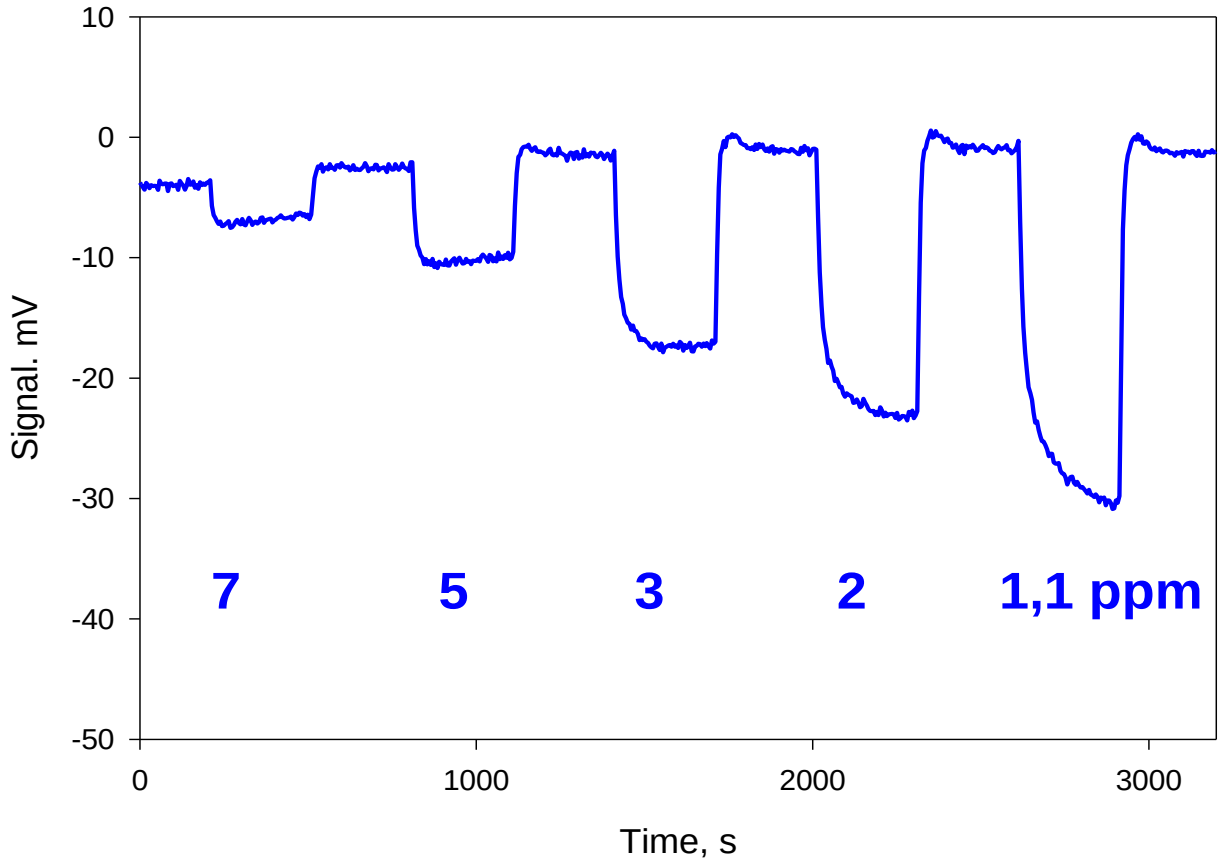
$$I \sim C_{F2}$$

MIS structure gas sensor with solid electrolyte layer



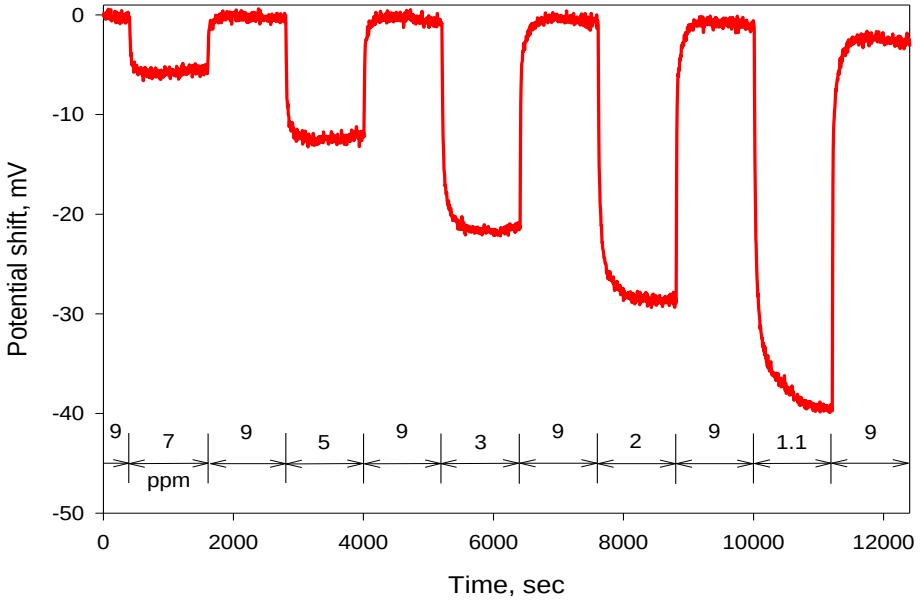


MIS structure response to F_2 concentration. Base line F_2 concentration is of 9 ppm.

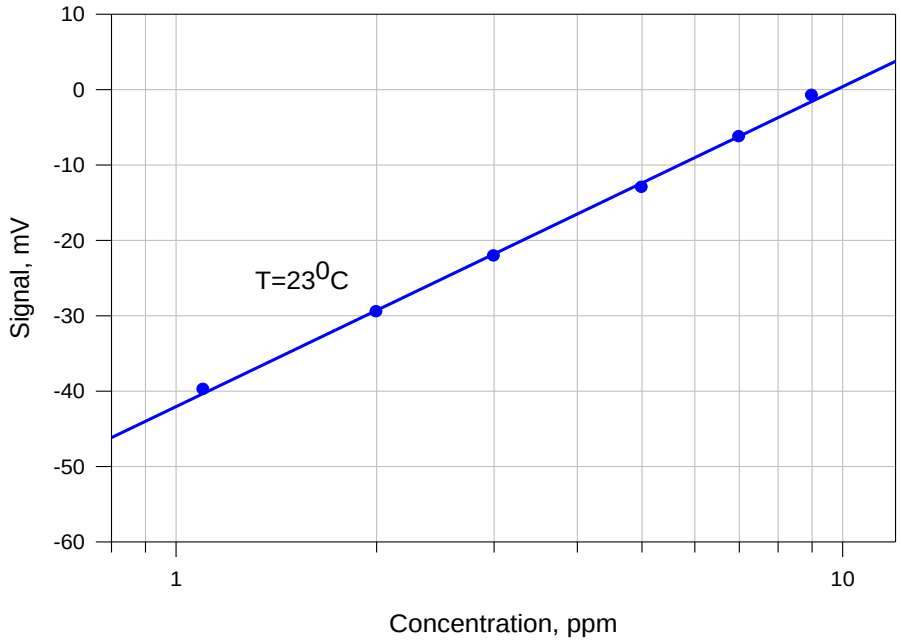


Average value of the sensitivity to fluorine at room temperature (RT) is of 28 ± 0,5 mV/dec.

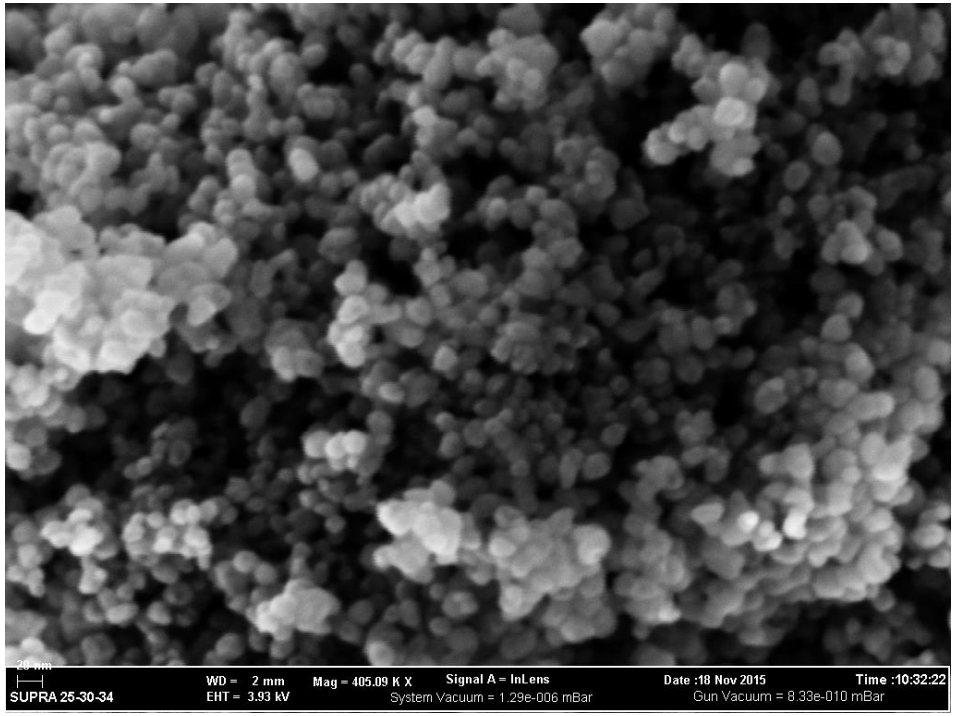
Response of the structure $Pt/LaF_3/SiO_2/SiC$ to HF at room temperature.

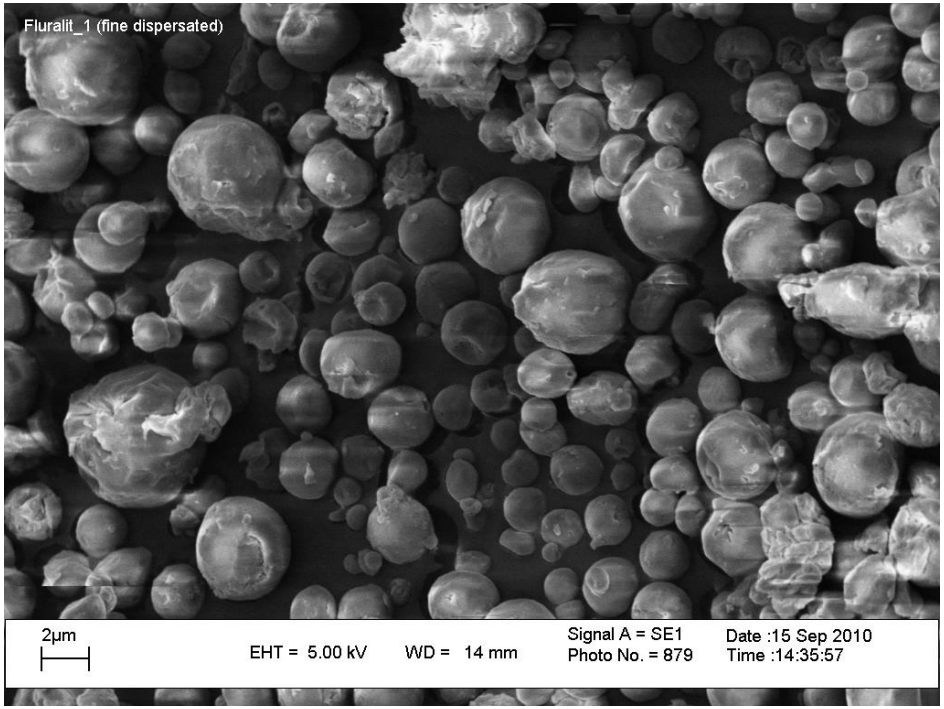


Sensitivity to hydrogen fluoride is of 45±3 mV/decade



Materials used in the experiment





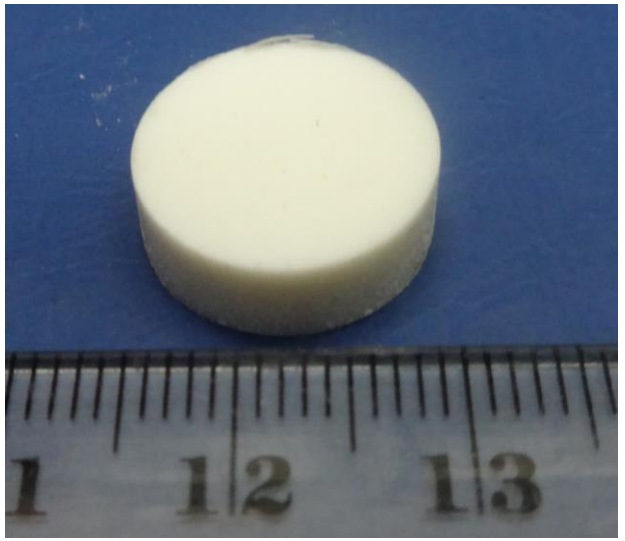
A **B**

(A) LaF3 + 3 wt. % SrF2 material used for the preparation of composite material.
(B) Teflon based mcroparticles (Fluralyte).

Fabrication of composite pellets

Mixing during 1 hour

Cold pressing



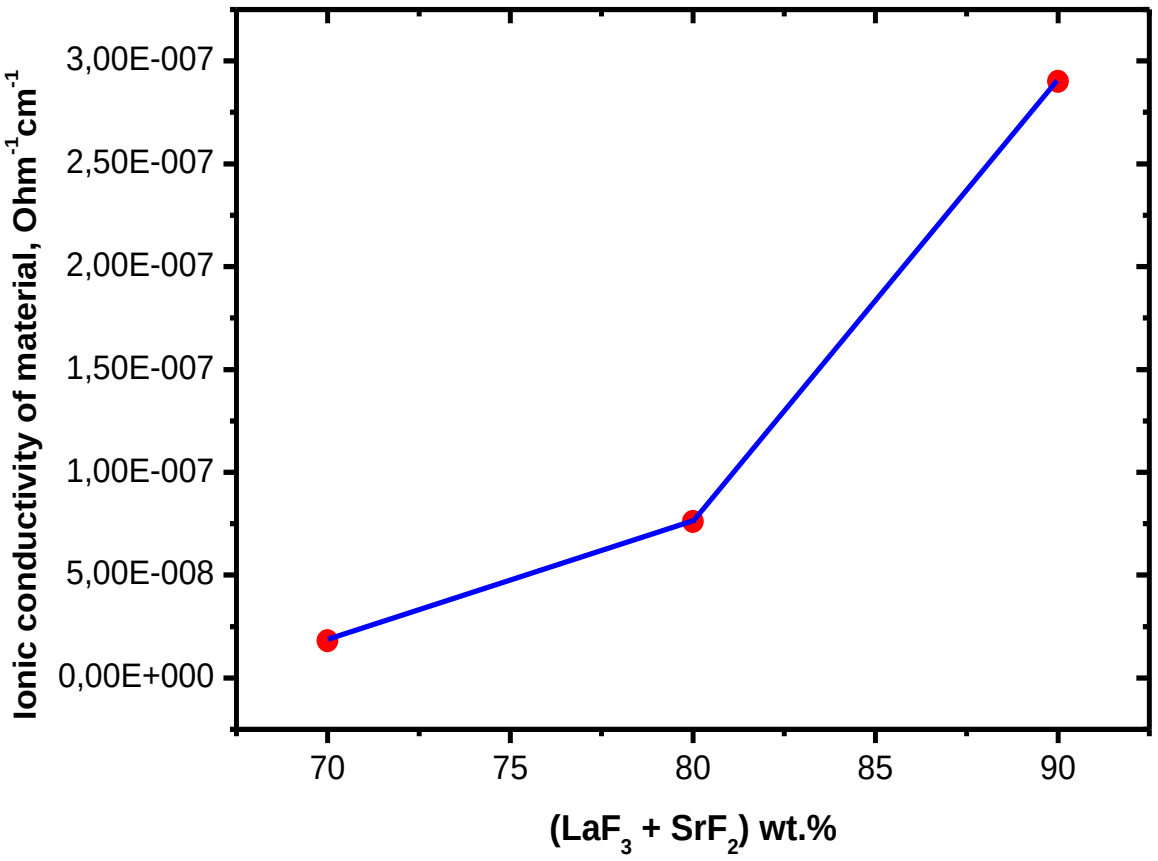
Pellet containing of LaF_3 + 3 wt. % SrF_2 (70, 80, and 90 wt. %) and Teflon

Sintering at 220ºC

Ionic conductivity of composite material

Electrode material at the measurement of ionic conductivity – graphite.

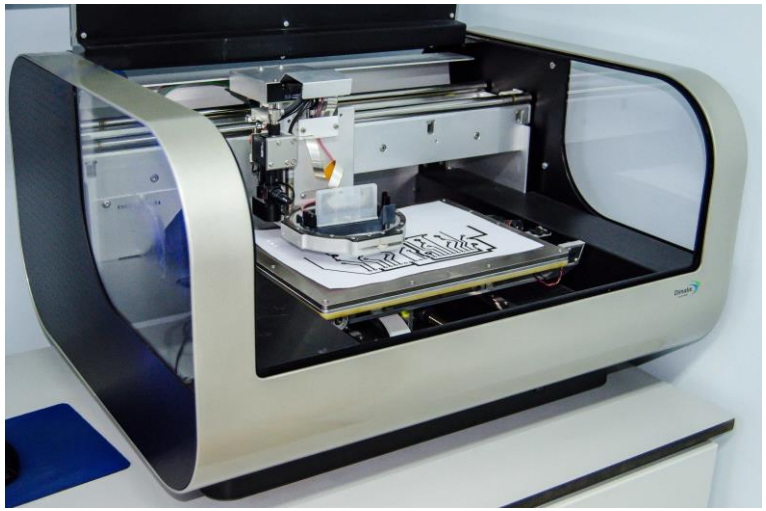
Gas sensor: reference electrode Sn/SnF_2; working (gas) electrode – printed or sputtered platinum.



Structure of gas sensor

- ***Gas sensor consists of composite pellet with Sn/SnF_2 reference electrode and Pt working (gas) electrode (printed or sputtered).***
- ***Main problem at the measurement of low concentration of HF (concentrations below 5 ppm) – slipping of sensor due to the formation of $LaFCO_3$. Removal of this passivating layer is possible by reverse current pulse leading to the generation of fluorine.***

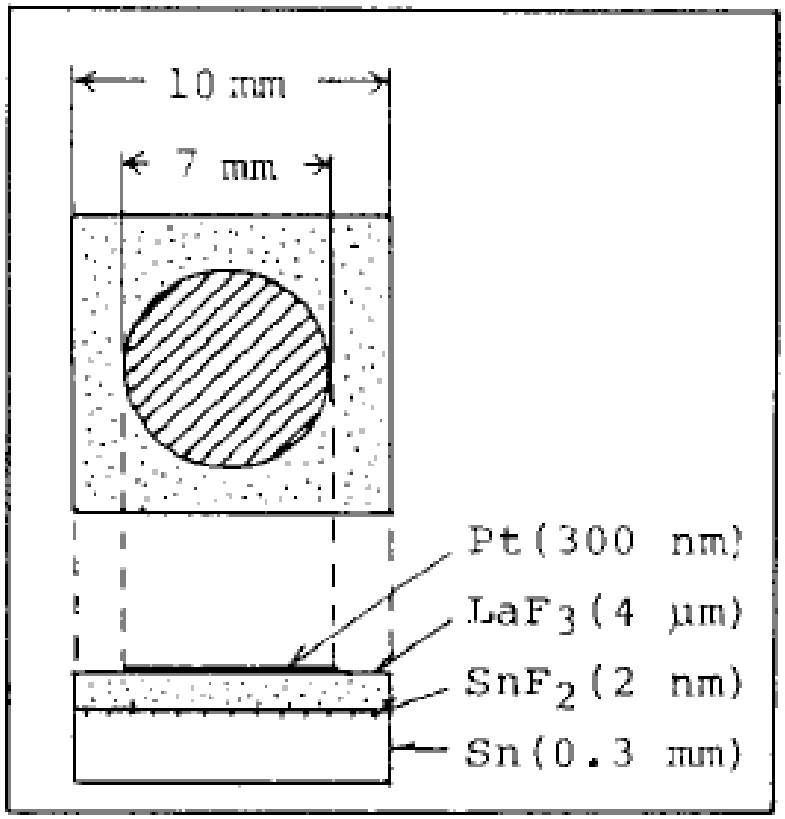
Prospective

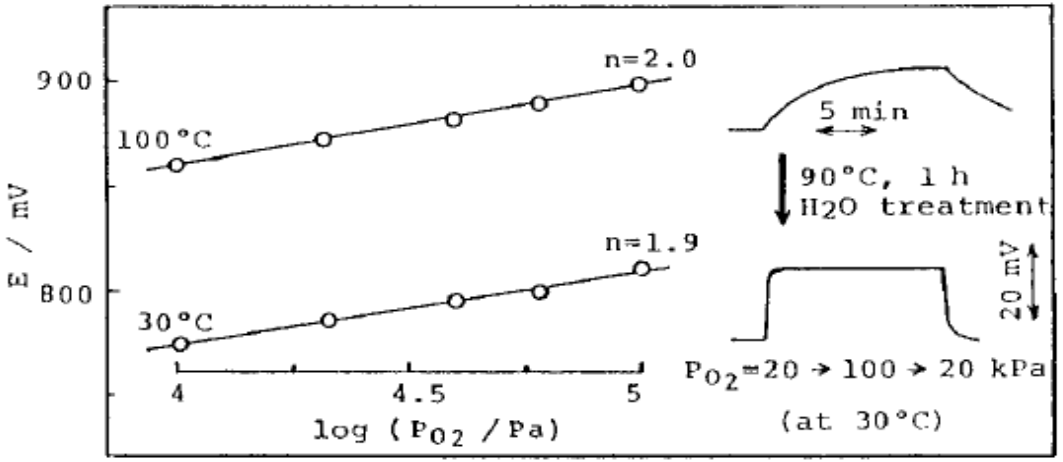


We will test the possibility to fabricate solid electrolyte as a film. This can be free-standing fil or the film deposited by printing technology.

With the conductance obtained now, the conductivity of 50 mm thick composite film is of 30 kOhm/cm^2. With ~ 3 V EMF for the system La/LaF_3/BiF_3 this corresponds to the exchange current of about 100 mA/ cm^2 – a typical value obtained at room temperature for this system.

Oxygen sensor





Structure and response of potentiometric sensor with sputtered LaF_3 layer

N. Miura et al. / LaF_3 sputtered film sensor for detecting oxygen at RT
Applied Surface Science 33/34 (1988) 1253–1259

Sensor application

- ***Analysis of low concentration of fluorine, hydrogen fluoride.***
- ***Analysis of volatile fluorine containing compounds (freons, fluorides of W, Mo, U, Pu, etc.). In this case the catalyst must be used to convert fluoride into HF.***
- ***Fluoride ion selective electrodes.***


THANK YOU FOR ATTENTION!