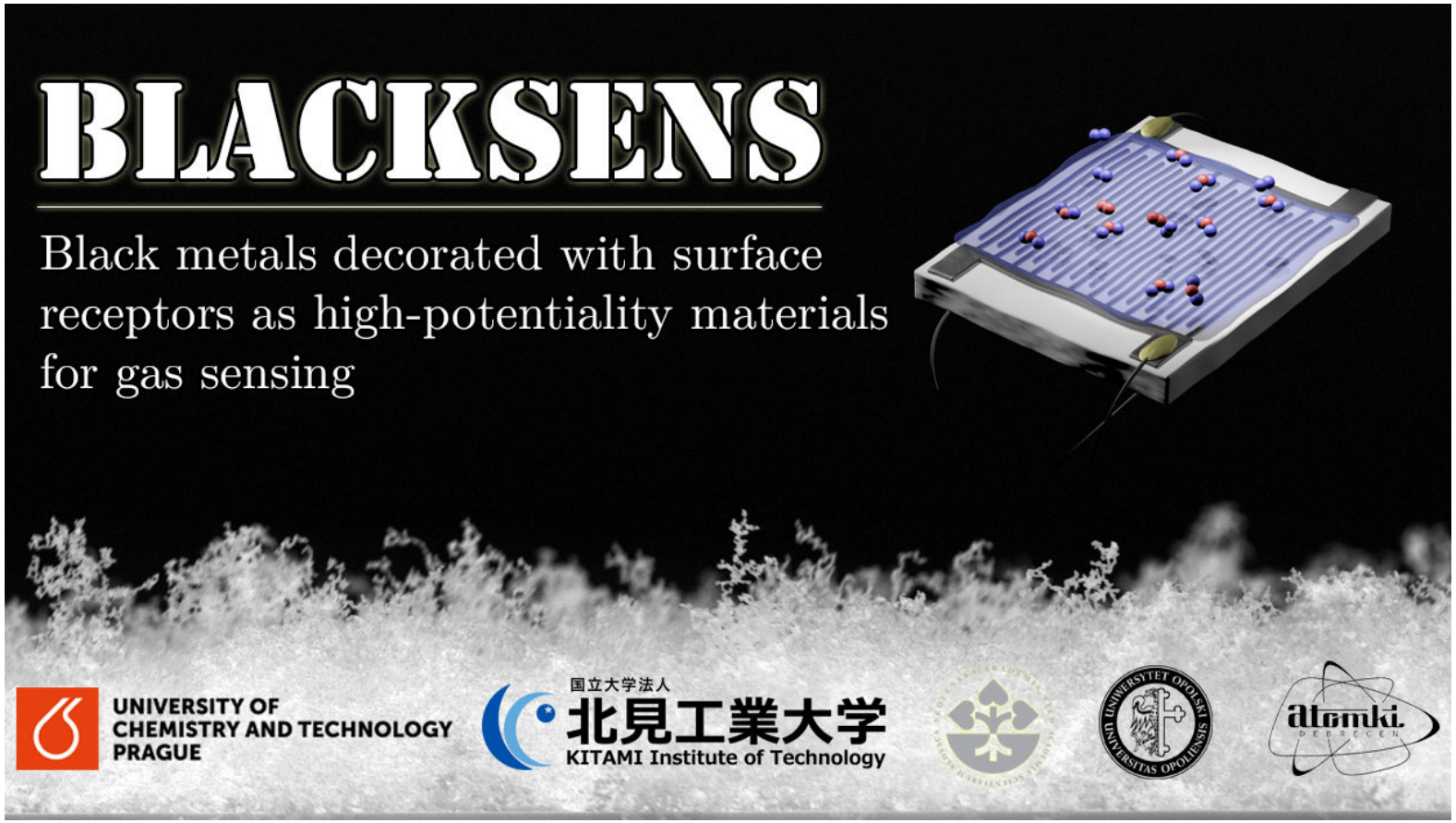
**Visegrad Group (V4) + Japan**

***- Innovation and Industry -***

***Joint Science Diplomacy Seminar***

11:30 9 March 2022




*Presenter : Prof. Midori Kawamura, JAPAN*

KITAMI Institute of Technology

SICORP
戦略的国際共同研究プログラム

# The Japanese groups are in Hokkaido

Prof. Mikito Ueda

Prof. M. Kawamura




Hokkaido is the northern most prefecture in Japan.

Access to Sapporo, Kitami:
1.5h flight from Tokyo

# Research groups of BLACKSENS

**Principal Project Leader**

| Czech Republic |
| --- |
| **Dr. P. Fitl**<br>Univ. of Chem. Tech. Prague (UCT Prague) |

**Secondary Project Leader**

| Japan |
| --- |
| **Dr. M. Kawamura**<br>Kitami Inst. of Tech. (KIT) |

| Japan |
| --- |
| **Dr. M. Ueda**<br>Hokkaido Univ. |

| Slovakia |
| --- |
| **Dr. M. Mičušík**<br>Polymer Institute of Slovak Academy of Sciences(PISAS) |

| Poland |
| --- |
| **Dr. G. Dydra**<br>Univ. Opole |

| Hungary |
| --- |
| **Dr. T. Fodor**<br>Institute for Nuclear Research (ATOMKI) |

# Research background of BLACKSENS

NOx is a pollutant that affects the human body and the environment, and organic nitrate is an explosive marker, so accurate detection is important.

We develop a low-cost sensor that can detect low-concentration NOx -based gases with high sensitivity at room temperature.

The sensor consists of
quartz crystal microbalance (QCM) , black metals (BM) and receptors

# Quartz Crystal microbalance (QCM) and Black metals

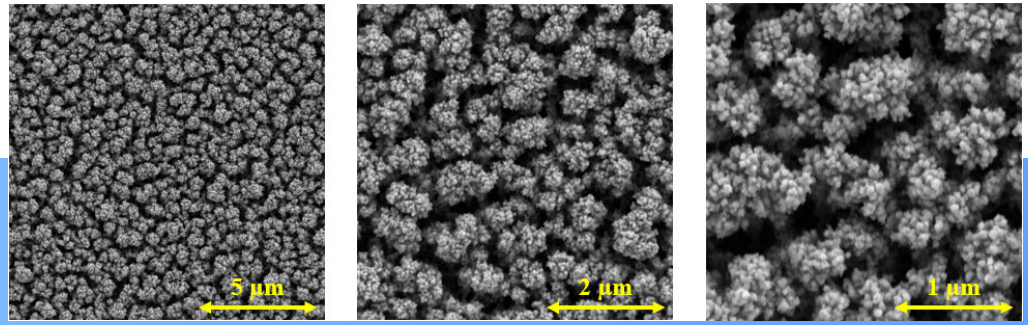
## QCM

- An AT-cut quartz crystal vibrates at a constant frequency when ac voltage is applied.
- Deposition/adsorption of substance → frequency decreases
- Detecting the frequency change → mass change of the substance

$$\Delta f = -\frac{2f_0^2}{A\sqrt{\rho_q \mu_q}}\Delta m$$

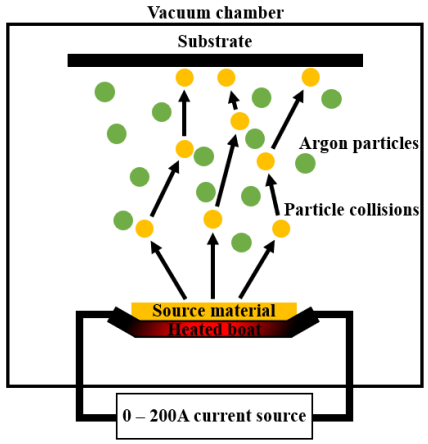
## Black metals (BM)

- Densely porous cauliflower-like surface structure, which is responsible for trapping incident light, resulting in the black color
- High potencial in the gas sensing device, due to the high surface to volume ratio, offering numerous bonding sites for gas analytes



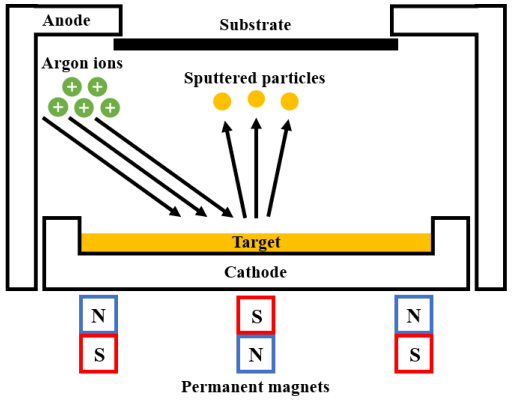
# Deposition techniques

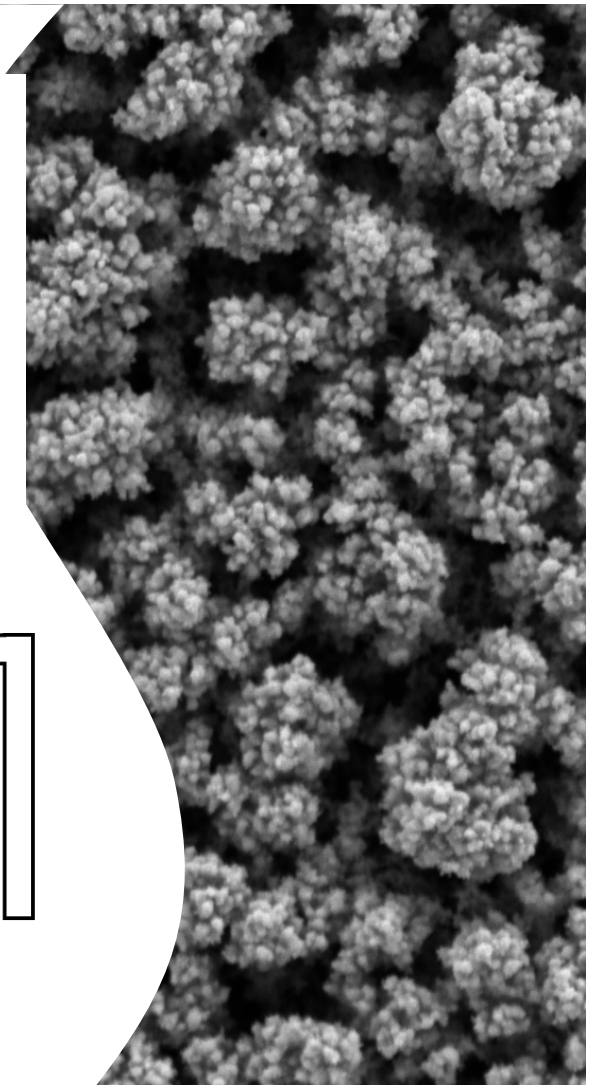
**Thermal evaporation**: Evaporation of the source material in the inert atmosphere of argon with pressure about hundreds of pascals. The evaporated material is losing its kinetic energy and stays on the substrate in arbitrary positions



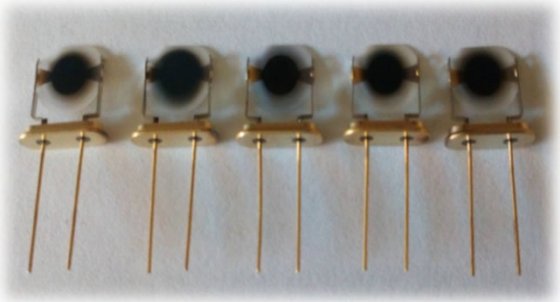

**Magnetron sputtering** :

the target material is bombarded by the argon ions. Sputtered particles then stick to the sustrate

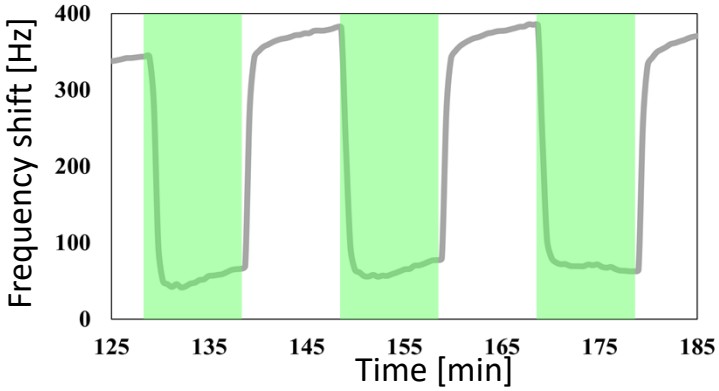


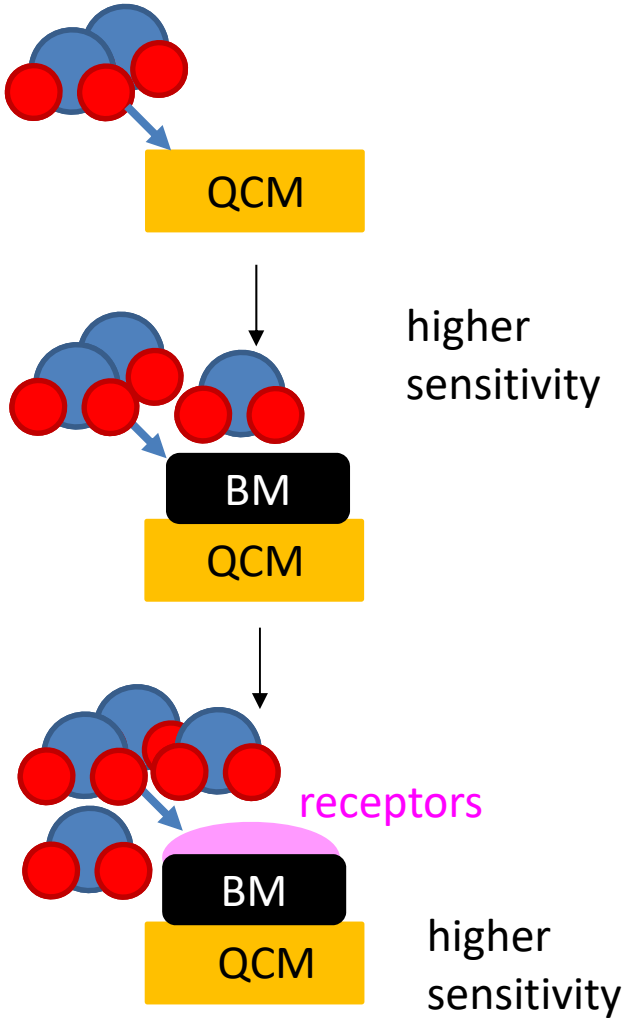



# BM on QCM Substrate



- Exposure to the gas analyte causes the resonant frequency shift of the QCM crystal.



# Research Goals

Aiming to improve sensor characteristics

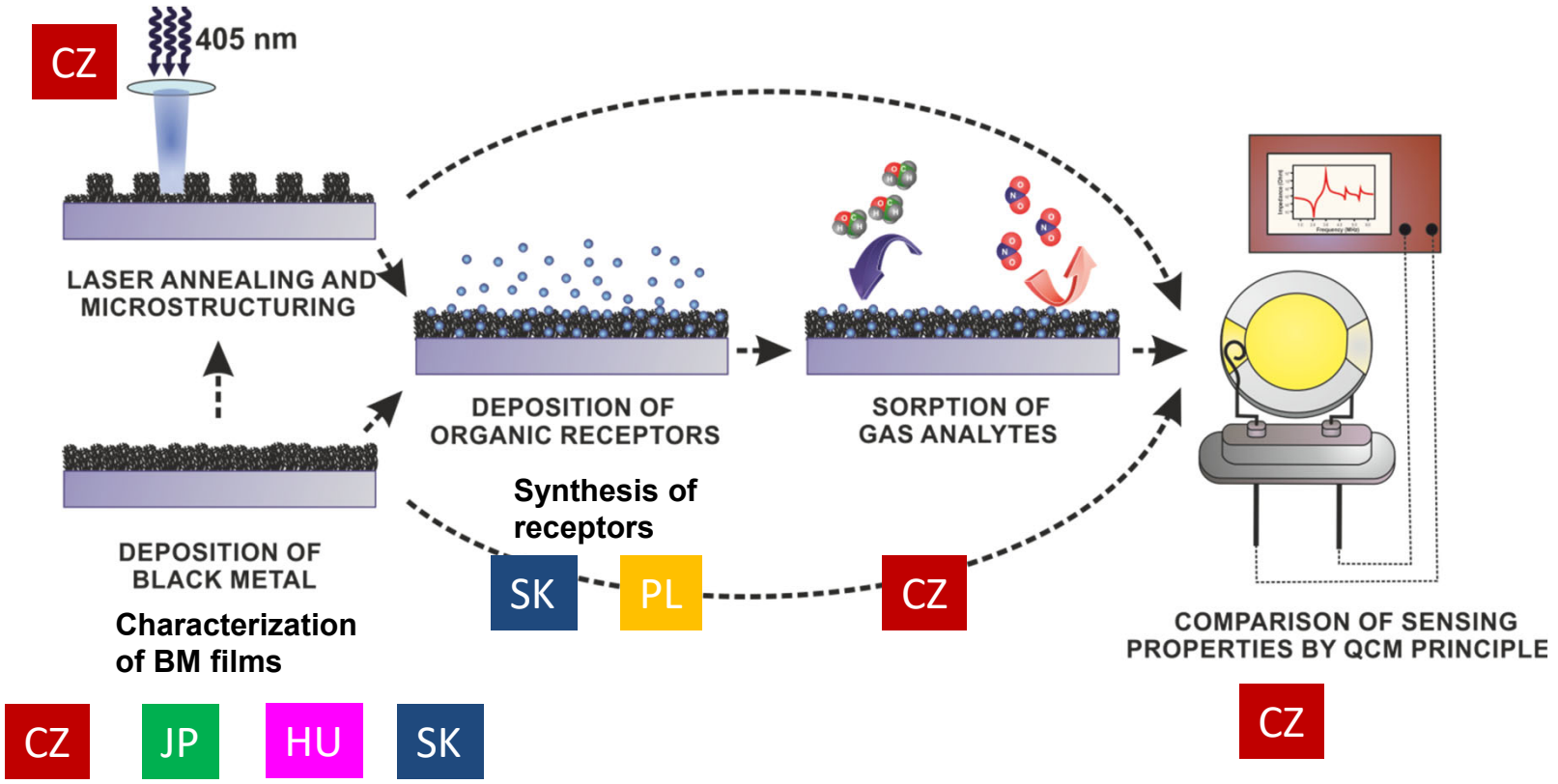
10 ppm $NO_2$ has been detected with BM films without receptors. Achieve the detection limit of 1ppm by the effect of receptors, etc.

Important items to achieve this goal:

1. porosity and stability of BM films
2. Selection of BM film constituent metals (and alloys)
3. Development of organic and inorganic surface receptors.

These explorations will be accomplished through V4-Japan cooperation.

# How to fabricate the QCM sensors



# Research groups of BLACKSENS

Principal Project Leader

Secondary Project Leader

| Czech Republic | Japan | Japan |
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| **Dr. P. Fitl**<br>Univ. of Chem. and Tech. Prague | **Dr. M. Kawamura**<br>Kitami Inst. of Tech. | **Dr. M. Ueda**<br>Hokkaido Univ. |

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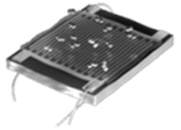
CZ

# UCT Prague Sensor Group

UNIVERSITY OF CHEMISTRY AND TECHNOLOGY PRAGUE

**Dr. Přemysl Fitl**

**Dr. Michal Novotný**



**Sensor Group**
http://sg.vscht.cz

- one of the research groups at the **Department of Physics and Measurements,** a part of **Faculty of Chemical Engineering**
- **11 members**

## Research

- **Preparation and characterization of thin film structures for chemical gas sensors** *(Black metals, Inorganic semiconductors, Organic semiconductors, Polymer Ionic Liquids, Composites and Nanocomposites)*
- **PVD, CVD, PLD processes**
- **Design and development of gas sensors and sensor substrates**
- **Security systems of early detection (chemical warfare agents and taggants of explosives)**
- **Industrial systems for detection of hazardous gases and vapors ($NO_2$, $NH_3$, CO...)**
- **Monitoring systems of environmental pollution**

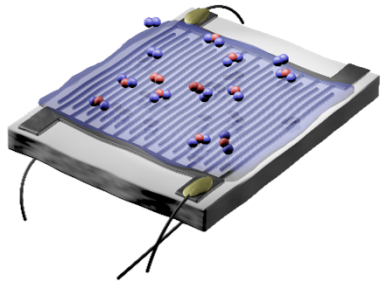
KITAMI Institute of Technology

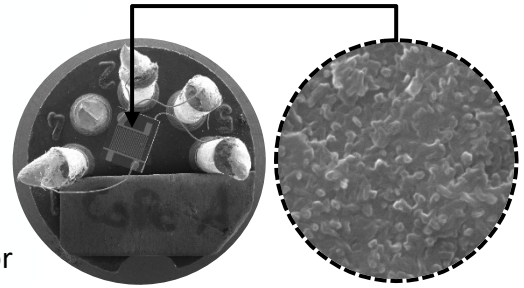
CZ

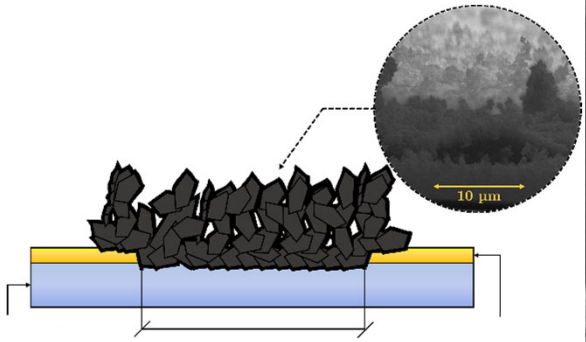
# Sensor Group

## Technologies + Analyses – gas sensing

- **Measurement of impedance in frequency range from 0,001 Hz up to 110 Mhz**
- **Measurement of DC resistance in range from 1μΩ up to 1T Ω**
- **Gas chromatograph with IMS detector, Gas analyzer with quadrupole mass filter**
- **Preparation of gas mixtures (permeation, gas mixing)**
- **QCM measurements**







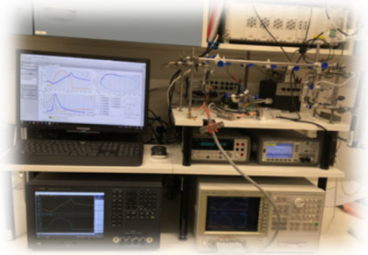

## Selected Projects – gas sensing

- **Czech Science Foundation (GACR)** project no. 22-14886S, Advanced chemoresistive device based on gas sensitive single-1D nanostructures (2022-2024)
- **Czech Science Foundation (GACR)** project no. 19-02804S, Nanostructured heterojunctions for chemiresistors (2019-2021)
- **Ministry of Industry and Trade of the Czech Republic**, project no. FV20350, Chemiresistors Based on Nanocomposite Layers for Gas Detection (2017-2021)
- **Ministry of the Interior of the Czech Republic**, project no. VI20192022155, Advanced semiconductor sensors for hazardous industrial gases (2019-2022)
- ***Ministry of Education, Youth and Sports*** *project no. LTC17058, Nano-Carbon Composite Materials for Thin Film Chemical Gas Sensors and Photovoltaics (2017-2020)*
- ***Czech Science Foundation*** *(**GACR**) project no. 17-13427S, Detection mechanisms on chemiresistors with a sensitive layer based on nanostructured oxides (2017-2019)*
- ***NATO Science for Peace and Security*** *project no. CEP-SPS NATO 984597, Solid state gas sensors against security and military threats (2014-2017)*

CZ

# Sensor Group

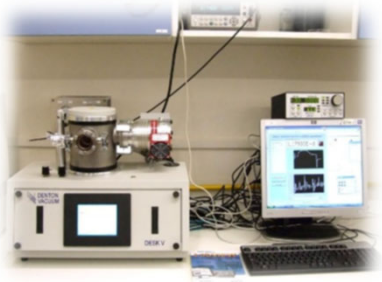
## Selected Equipments



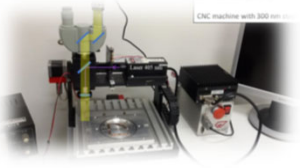
*In-house developed systems for **measurement of QCM sensor properties**, Impedance analysers 4294A and E4990A*

*In-house developed systems for **measurement of sensor properties**, Electrometer Keithley 6517A and Keysight 34465A - precise measurement of high resistance materials with in-house fixtures with triaxial interconnection*

***HV – Pulsed laser deposition system***



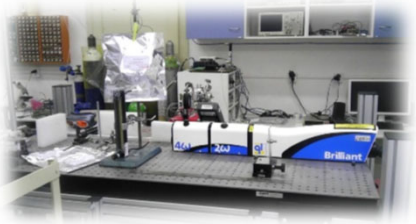
*Denton DeskV TSC **DC Magnetron sputtering** deposition system*



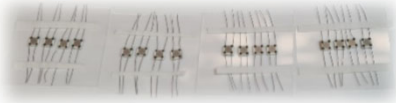
***Laser-Induced Forward transfer system**. System is based on Micro-CNC machine (Gravos GV-21) with resolution ~300 nm with diode laser wavelength of 405 nm, with power up to 200 mW*

***HV - Deposition system** combining molecular evaporator (Creaphys DE-FR/2.2), thermal boat evaporator and pulsed laser deposition*

***UHV - Deposition system** combining two molecular evaporators and one boat evaporator, simultaneous deposition of various materials*



***Nd:YAG Laser** Quantel Brilliant 4th harmonics – 266 nm, 4ns, 45mJ*



***Chemiresistor substrates** KBS4 developed in cooperation with company TESLA Blatna*

*VarioCAM HD **thermal camera** with microscope lens – resolution ~ 35µm*

***Quantum Design PPMS** (Physical Property Measurement System) with modules for measurement of electro-transport and magnetic properties in temperature range 1.85-400 K and magnetic fields up to 9T*

JP

# Kitami Institute of Technology

- National university corporation established in 1960.
- 2,000 students from all over Japan and abroad.

## Thin Film Electronic Materials Lab.

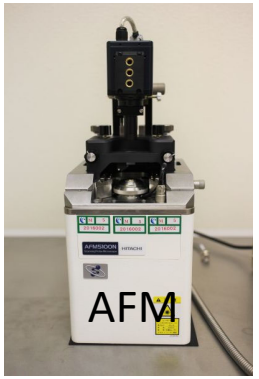
M. Kawamura

Prof. Y. Abe

Assoc.Prof. Kiba

vacuum evaporator

sputtering apparatus




OLEDs, smart window, low-E coating, etc.

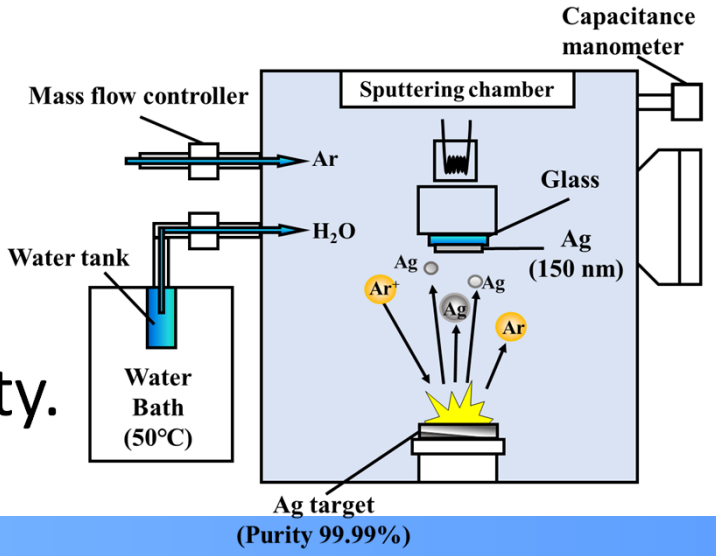
JP

# Our tasks

- Preparation of BM film by PVD method
- Development of a new BM film fabrication process, especially by deposition at liquid nitrogen temperature.

The substrate can be cooled down to liq.N2 temp.
Water vapor can be introduced into the chamber.

- Characterization of BM films
- Determination of the relationship between the physical properties of various BM films and their porosity.

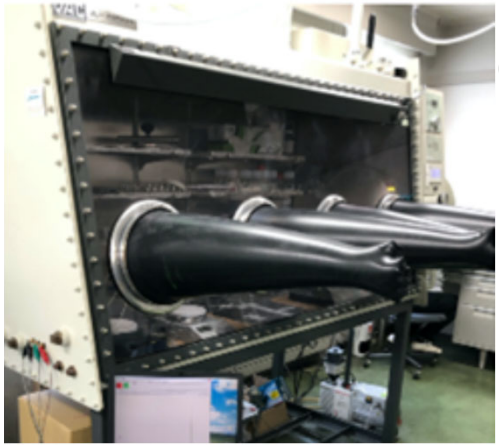


JP

# Hokkaido University, Faculty of Eng.

established in 1876.  18,000 students are enrolled.

## Fabrication of BM Films by Electrochemical Methods




Co-deposition of Al and Au using
non-aqueous liquids
(ionic liquids, molten salts)

Ar atmosphere
glove box

Porous film


Selective dissolution of Al

## Comparison of properties with BM films prepared by PVD method

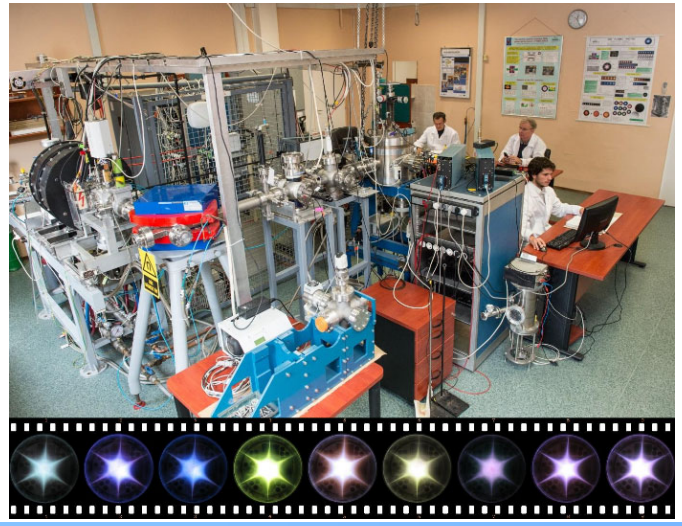
Prof. Mikito Ueda
Environmental Materials Science lab

HU

# Institute for Nuclear Research (ATOMKI)

Established in 1954 by Prof. Sándor SZALAY.

- Number of researchers 100, total number of staff around 200
- PhD students connected to the educational program of University of Debrecen (UD)



Electron Cyclotron Resonance (ECR) laboratory

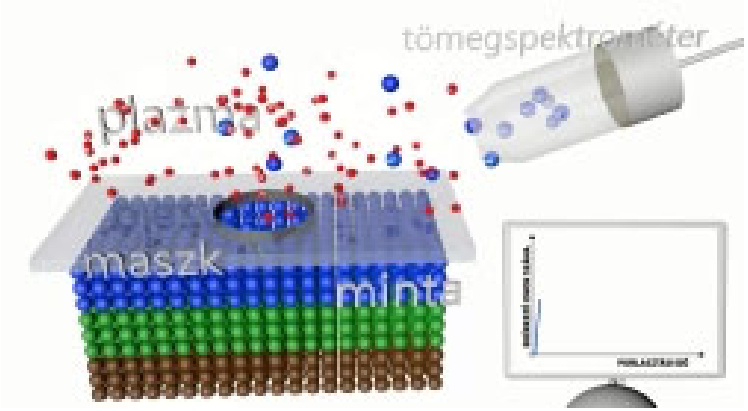
## Laboratory of Materials Science

Dr. T. Fodor

Dr. A. Csik

HU

## ➢ **S**econdary **N**eutral **M**ass **S**pectrometer (SNMS)




No matrix effect  Depth resolution < ~1 nm

- performing SNMS depth profiling of the samples
- morphological, cross-sectional and structural analysis

- to determine of relationship between observed sample structure and sample preparation procedures
- to give the feedback how to modify and improve the sample preparation procedures
- to provide output (studies) for colleagues to improve deposition procedures

PL

# Opole Univ. Institute of Chemistry

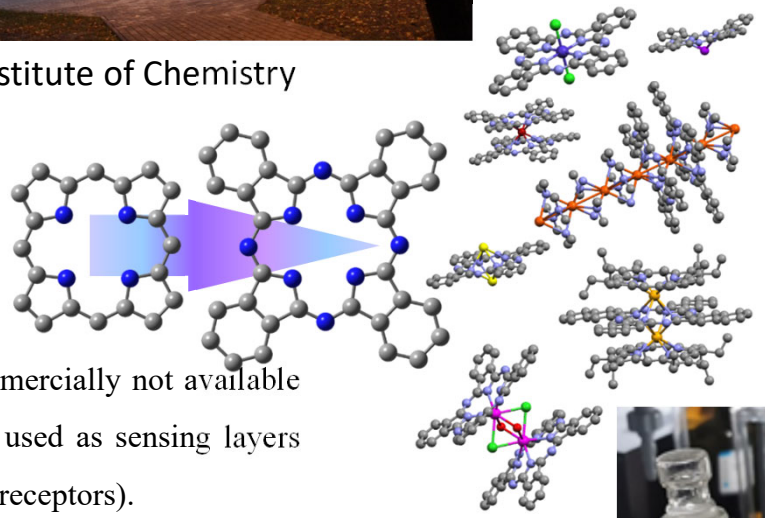
UNIVERSITY OF OPOLE
EUROPEAN UNIVERSITY

University of Opole Headquarters

Institute of Chemistry

Dr. Gabriela Dyrda

Prof. Rudolf Słota



The main task is to synthesize a series of commercially not available phthalocyanine and porphyrin materials, to be used as sensing layers deposited on black metal thin films (*i.e.* surface receptors).

Characterization include UV-VIS-NIR absorption and emission spectroscopy, FTIR, SEM/EDS, AFM, DSC, HPLC-GC, GC-MS. Photochemical activity are investigated.

First, sandwich phthalocyanine complexes including lanthanide metals will be prepared.

KITAMI Institute of Technology

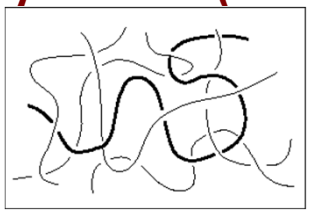
SK

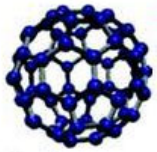
# Polymer Institute of Slovak Academy of Sciences (PISAS)


## Department of Composite Materials

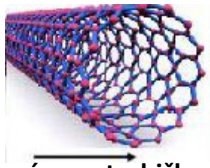
Dr. Matej Mičušík
and colleagues

**Polymer + (nano)particles (0D, 1D, 2D, 3D)**

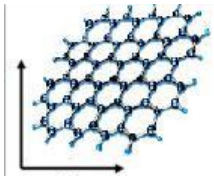




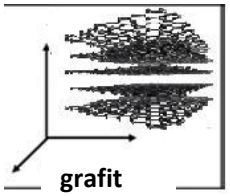
fulerén,
kvantové bodky
(perovskit, uhlík)



uhlíkové nanotrubičky



MXén,
grafén, $MoS_2$



grafit

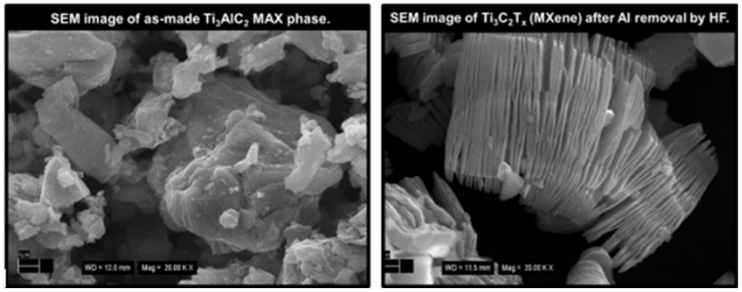
**hybrids with conducting polymers (popypyrrole)**

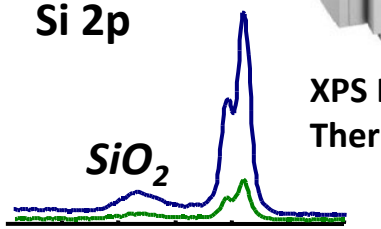
KITAMI Institute of Technology

SK

# Synthesis and Characterization

- **Preparation of 2D nanosheets of exfoliated 2D nanomaterials (MXene, graphene).**

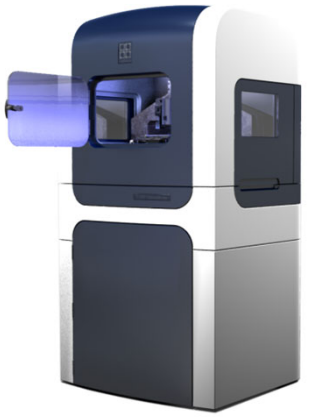



**XPS K-Alpha**
**ThermoFisher Scientific**

- **surface and interface properties of prepared BM film by XPS.**

- **nanomechanical properties and surface morphology of prepared heterostructured BM films will be studied by Nanoindentation.**



**Nanoindentor HysitronTl-750**

We hope to achieve synergy through our collaboration to achieve our research goals and to promote networking among researchers.

http://blacksens.vscht.cz/

JP CZ HU PL SK

*Please contact them.*

**Dr. Přemysl Fitl**

**Dr. Michal Novotný** UCT Prague (CZ)

**Acknowledgements**

We acknowledge for support project No. JP22420 from the International Visegrad Fund, JST SICORP Grant Number JPMJSC2108, Japan.

KITAMI Institute of Technology

国立研究開発法人 科学技術振興機構

Visegrad Fund