# Plasmatic Technologies (RP 5)

**Zdeněk Hubička**

RA1- R&D of advanced low temperature plasma systems for thin film polycrystalline materials - Z. Hubička

RA2 - Plasma diagnostics, optimization of plasma deposition systems, and monitoring of deposition processes - M. Čada

RA3 - Plasma methods of preparation of thin metallic and intermetallic layers - J. Lančok

RA4 - Thin-film chemical sensors - M. Novotný

RA5 – Optical materials-plasmon structures - J. Bulíř

RA6 – Structures exhibiting a combination of ferromagnetic properties - M. Tjunina

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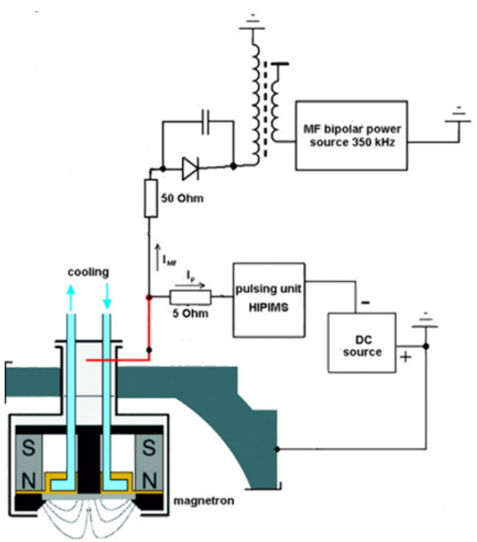
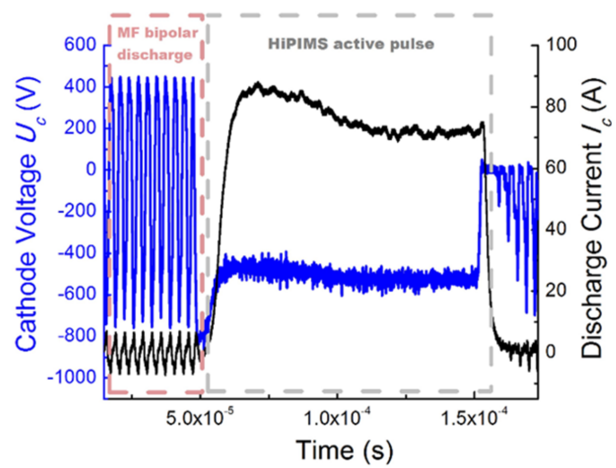
# RA1- R&D of advanced low temperature plasma systems for thin film polycrystalline materials - Z. Hubička

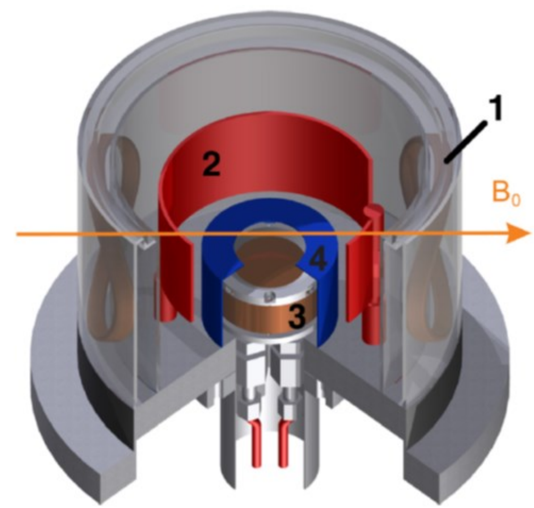
## Hybride HiPIMS deposition sources

-combination of HiPIMS and other plasma sources to optimise deposition, tailor thin film properties.

- hybrid HiPIMS - suppression of HiPIMS drawbacks.
- working at lower pressure, increase of deposition rate, increase of energy of ions, change of crystallographic phase.




J. Olejníček, Z. Hubička, Š. Kment, M. Čada, P. Kšírová, P. Adámek, I. Gregora., SCT 232 (2013) 376.

*V. Stranak, A.-P. Herrendorf, S. Drache, M. Cada, Z. Hubicka, M. Tichy, and R. Hippler, Appl. Phys. Lett. 100, 141604 (2012)*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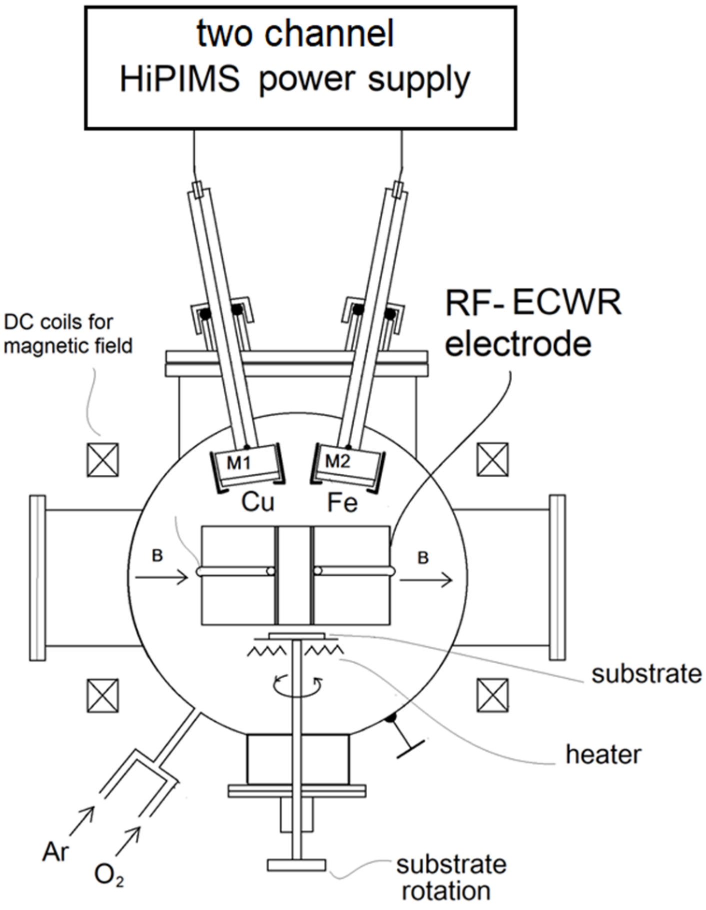
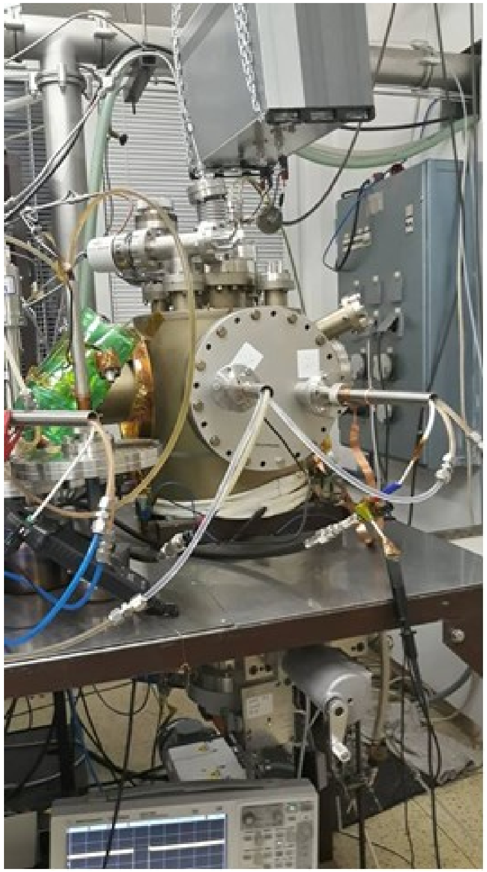
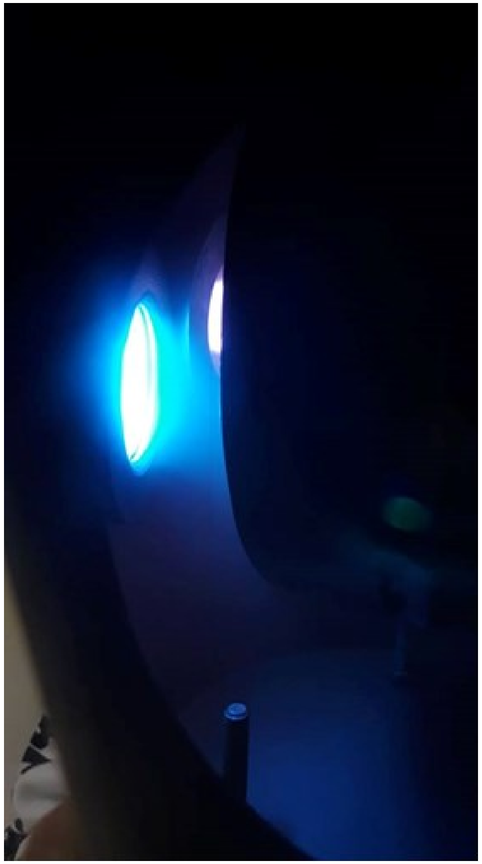
## RA1- R&D of advanced low temperature plasma systems for thin film polycrystalline materials - Z. Hubička

Semiconducting p-type copper copper oxide and iron oxide thin films deposited by hybrid
r-HiPIMS+ECWR magnetron plasma system





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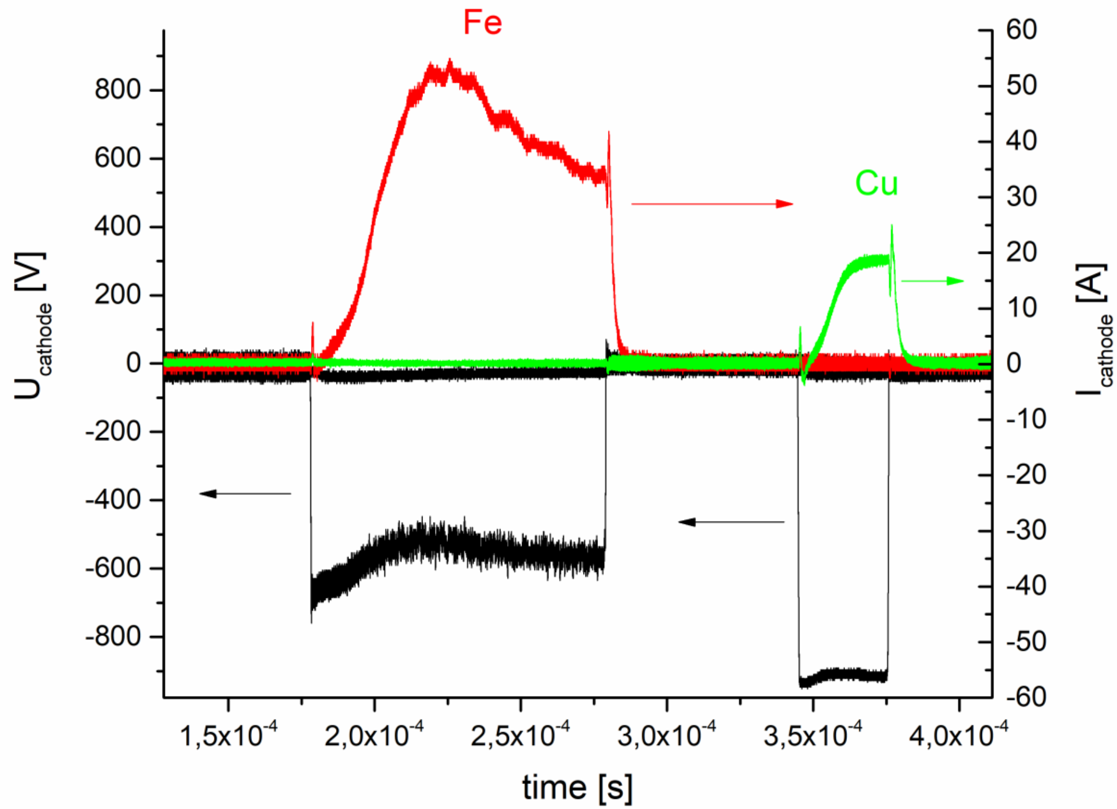


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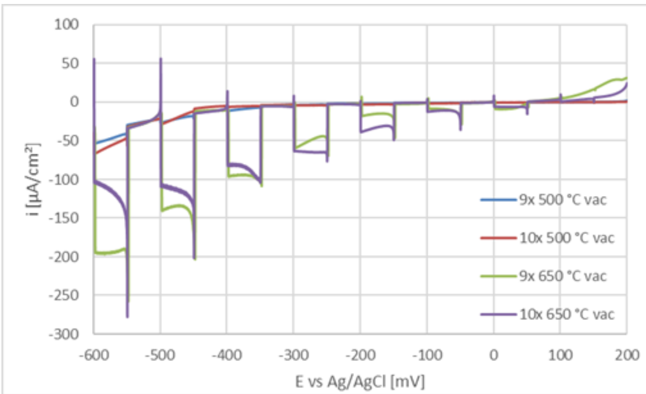
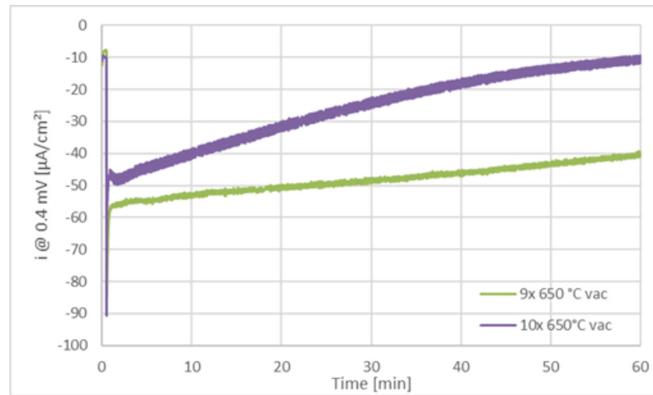
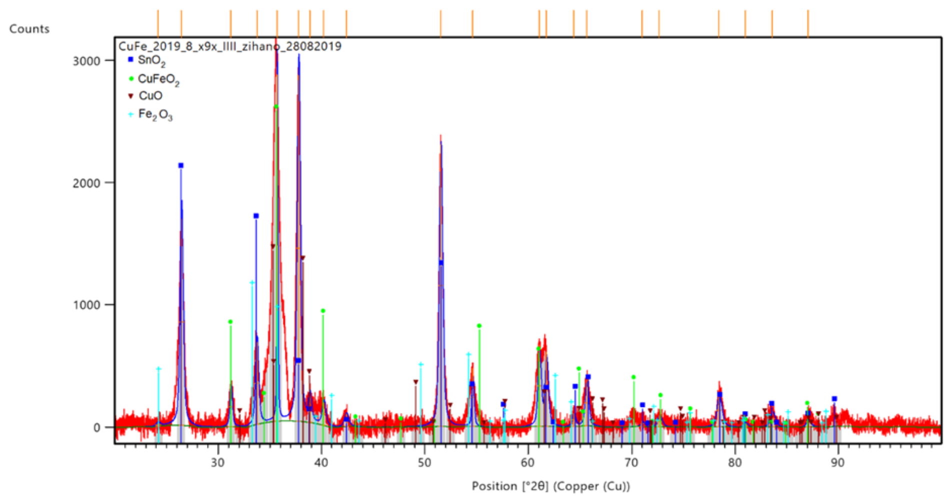
# Semiconducting p-type copper iron oxide thin films deposited by hybrid r-HiPIMS+ECWR magnetron plasma system

$CuFeO_2$ delafossite phase should be stable in PEC process (AM1.5 100 $mW/cm^{-2}$)

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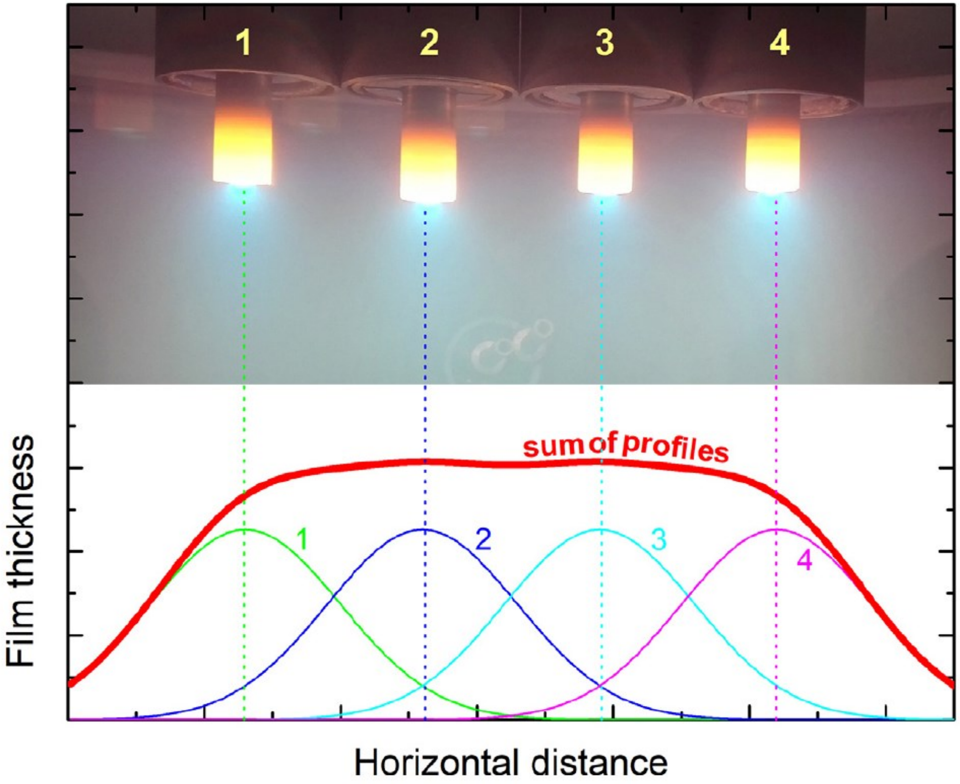
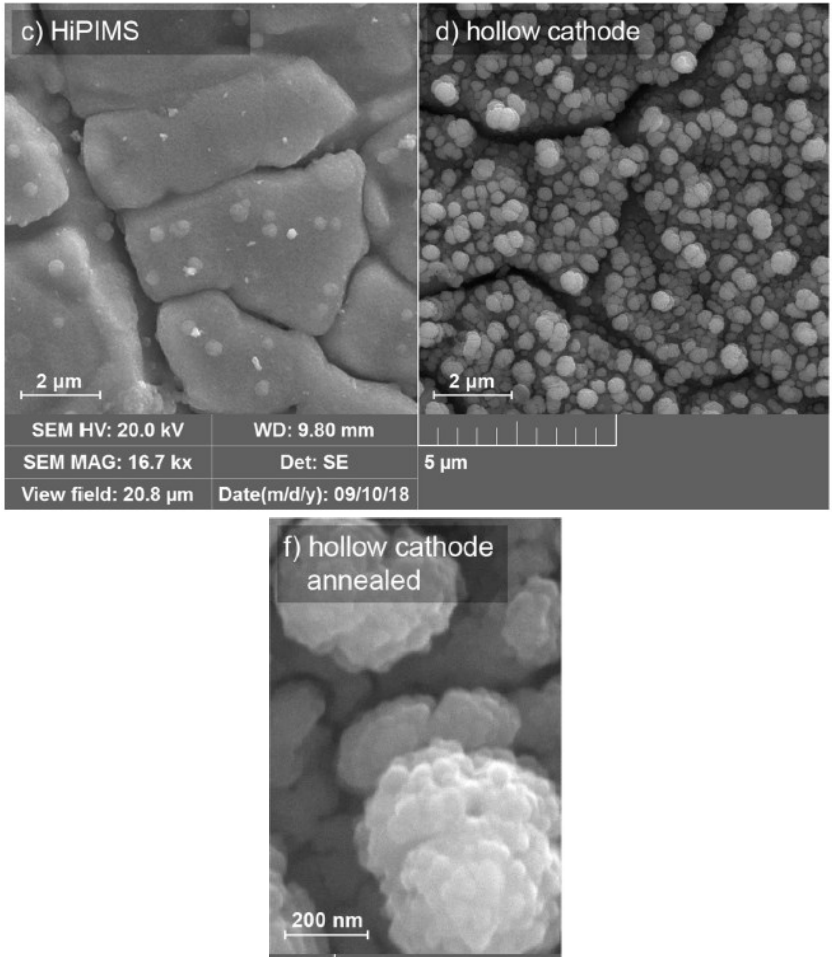
# $Co_3O_4$ thin films prepared by hollow cathode discharge

- $Co_3O_4$ thin films for catalytic applications (large surface area)





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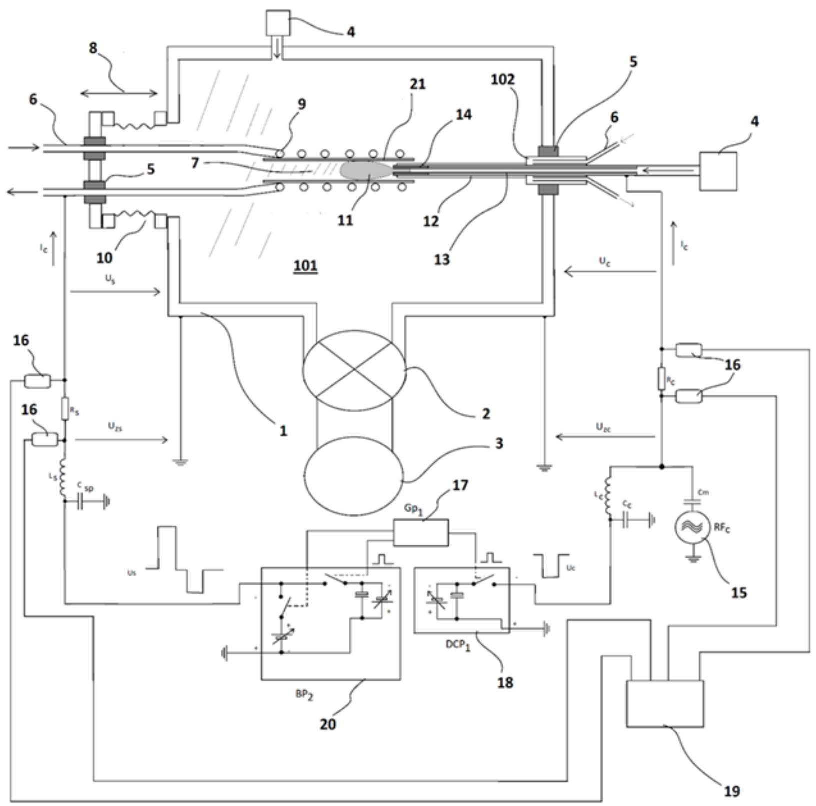
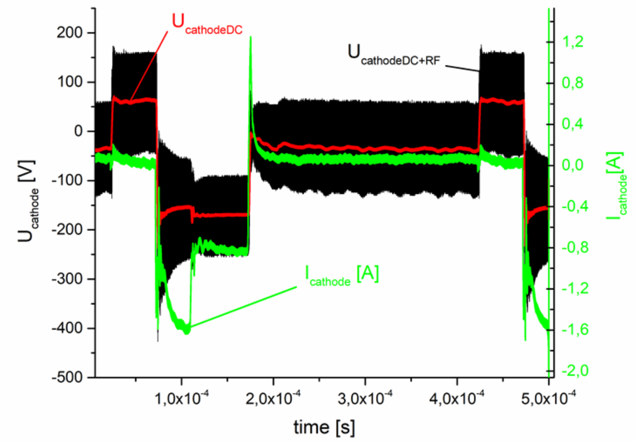
# Thin films deposited inside tubes

Z. Hubička, M. Čada, P. Kšírová, M. Klinger, A method of generating low temperature plasma, a method of coating the inner surface of hollow electrically conductive or ferromagnetic tubes and the equipment for doing this,  PV-2018-206307842, PCT/CZ2019/050019,  WO 2019/210891 A1.

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# Outputs RA1

**published:**

1) Z. Hubička, M.Zlámal, M.Čada, Š.Kment, J.Krýsa, Photo-electrochemical stability of copper oxide photocathodes deposited by reactive high power impulse magnetron sputtering Catal. Today 328 (2019) 29 - 34.

2) J. Olejníček, J. Šmíd, R. Perekrestov, P. Kšírová, J. Rathouský, M. Kohout, M. Dvořáková, Š. Kment, K. Jurek, M. Čada, Z. Hubička, Co3O4 thin films prepared by hollow cathode discharge Surf. Coat. Tech. 366 (2019) 303 - 310.

3) R. Perekrestov, A. Spesyvyi , J. Maixner, K. Mašek, O. Leiko, I. Khalakhan, J. Maňák, P. Kšírová, Z. Hubička, M. Čada, The comparative study of electrical, optical and catalytic properties of $Co_3O_4$ thin nanocrystalline films prepared by reactive high-power impulse and radio frequency magnetron sputtering, Thin Solid Films 686 (2019) 137427.

4) Z. Hubička, M. Čada, P. Kšírová, M. Klinger, A method of generating low temperature plasma, a method of coating the inner surface of hollow electrically conductive or ferromagnetic tubes and the equipment for doing this, PV-2018-206307842, PCT/CZ2019/050019, WO 2019/210891 A1.

**submitted:**

5) Z. Hubička, M. Zlámal, J. Olejníček, D. Tvarog, M. Čada, J. Krýsa, Semiconducting p-type copper iron oxide thin films deposited by hybrid r-HiPIMS+ECWR and r-HiPIMS magnetron plasma system, Coatings (submitted).

6) Z. Hubička, M. Čada, A. Kapran, J. Olejníček, P. Kšírová, M. Zanáška, P. Adámek, M. Tichý, Plasma Diagnostics in reactive High Power Impulse Magnetron Sputtering System working in Ar+H2S Gas Mixture, Coatings (submitted).

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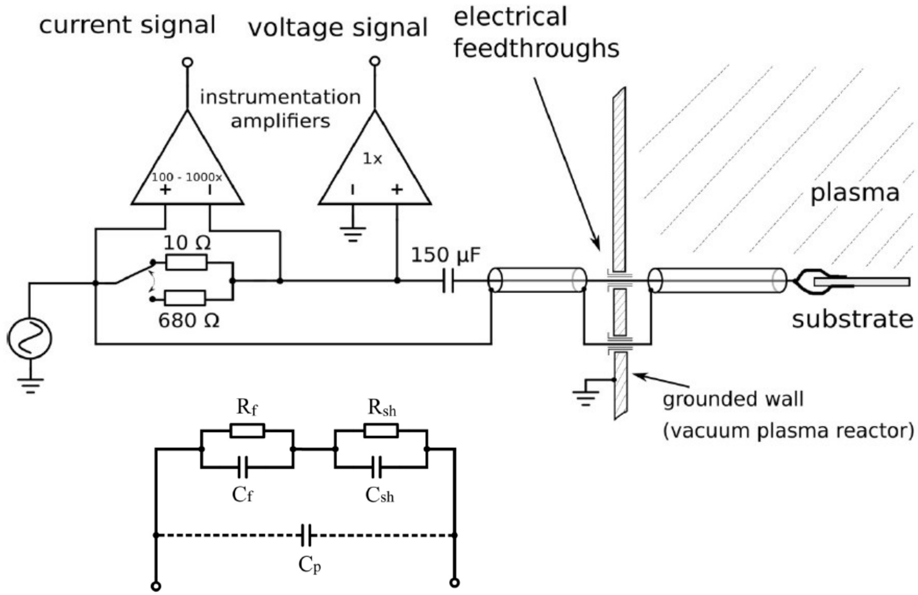
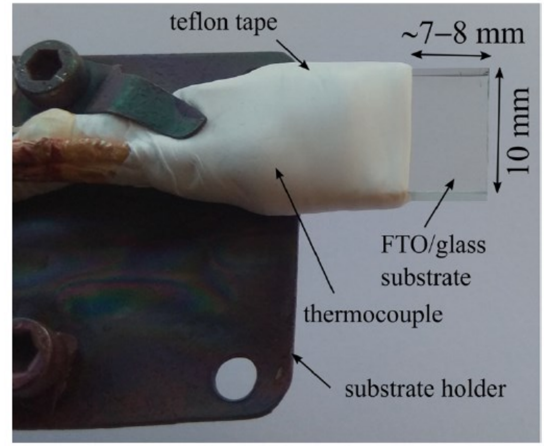
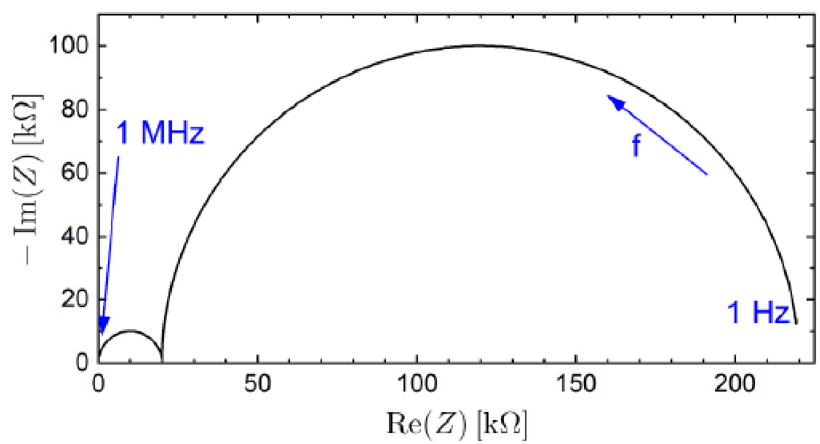
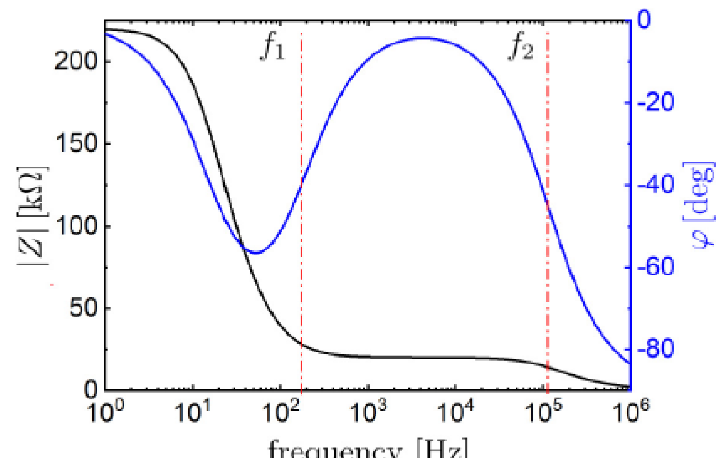
# In-situ impedance spectroscopy of a plasma-semiconductor thin film system during reactive sputter deposition

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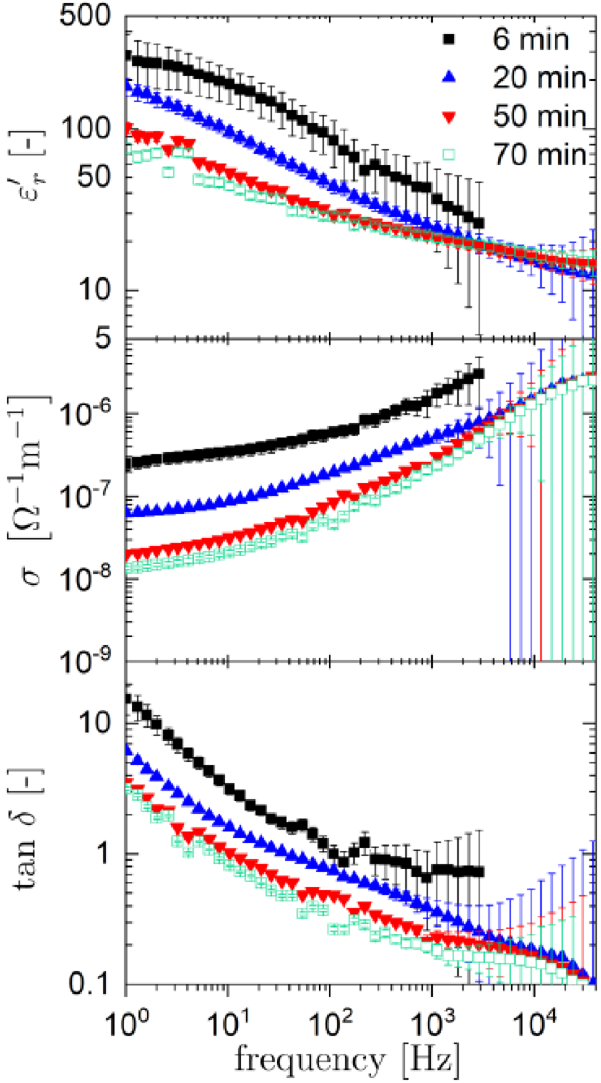


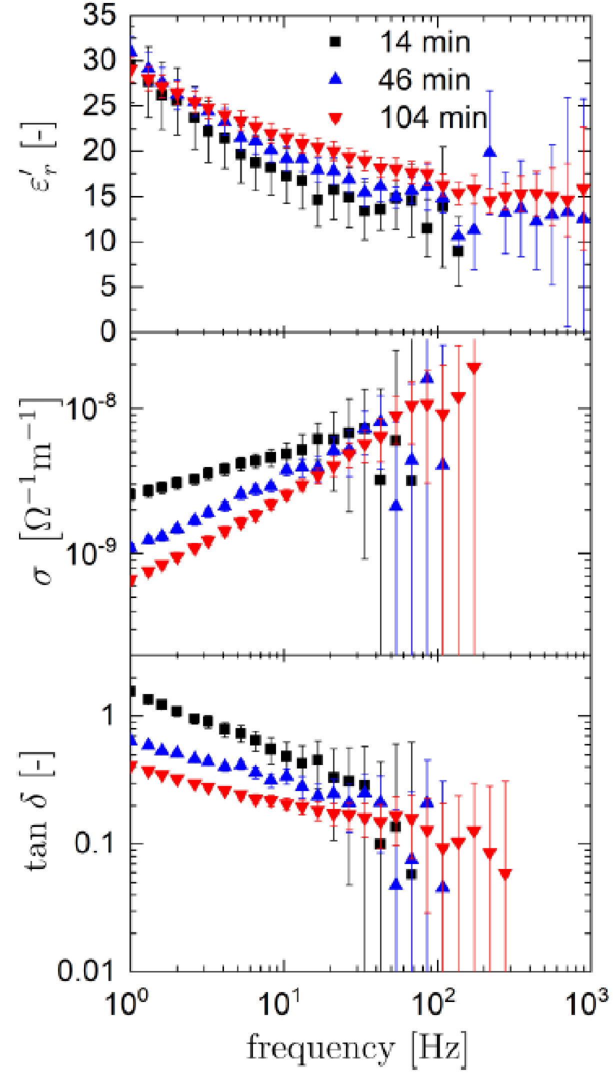



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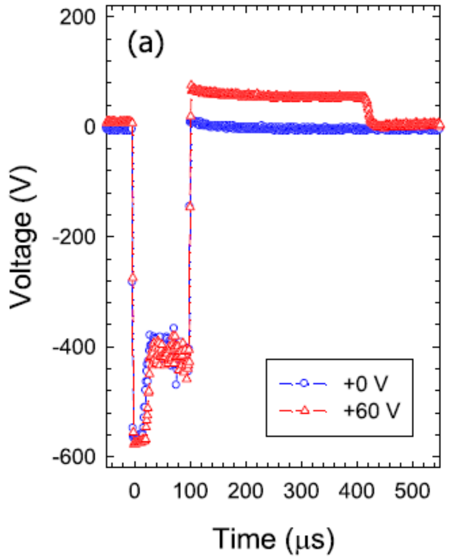
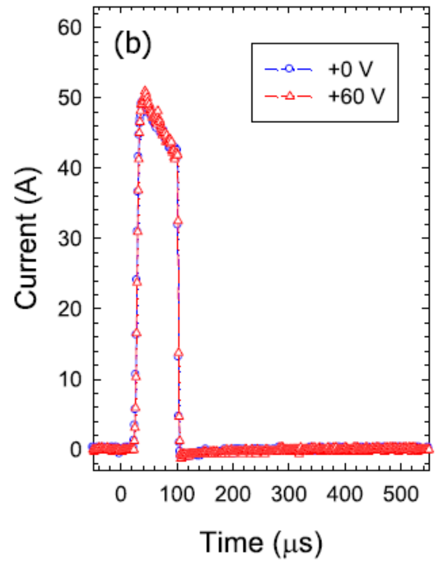
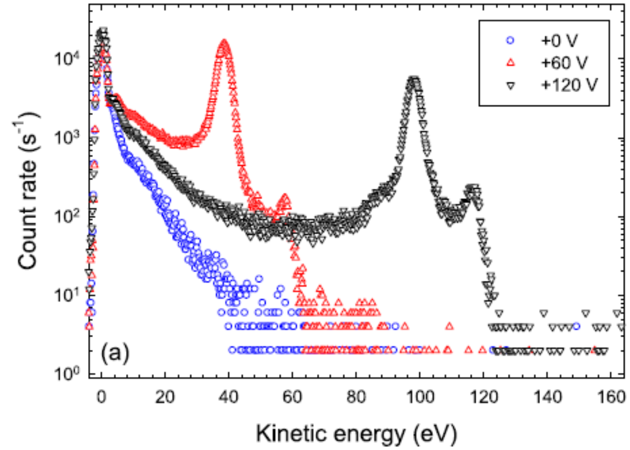
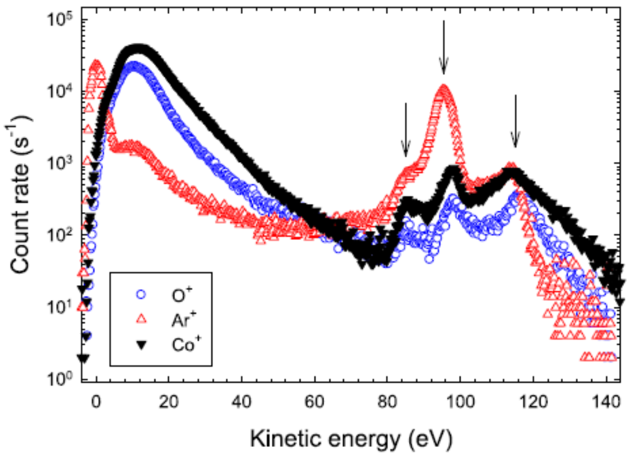
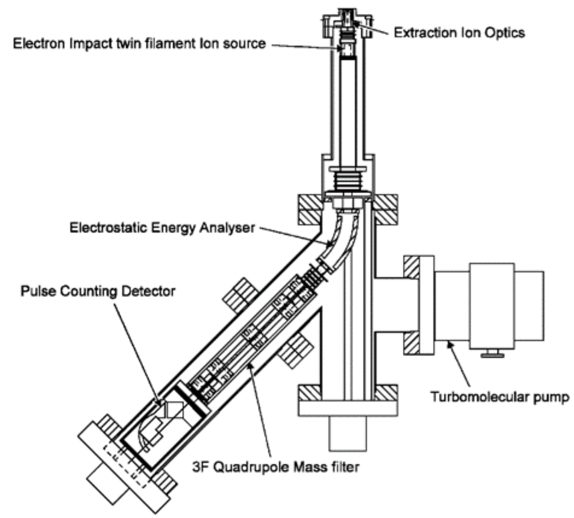
# Plasma diagnostics in bi-polar reactive HiPIMS deposition of $Co_3O_4$ thin films.



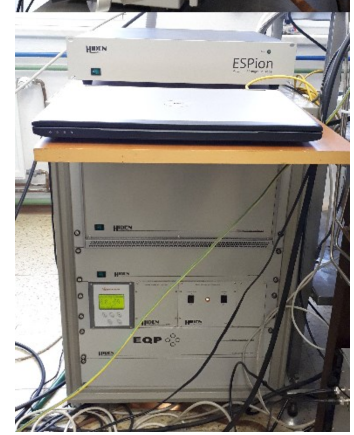





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**Outputs RA2**
**published:**

1) M. Zanáška, P. Kudrna, M. Čada, M. Tichý, Z. Hubička, In-situ impedance spectroscopy of a plasma-semiconductor thin film system during reactive sputter deposition, J. Appl. Phys. 126 (2019) 023301.

2) R. Hippler, M. Čada, V. Straňák, Z. Hubička, Time-resolved optical emission spectroscopy of a unipolar and a bipolar pulsed magnetron sputtering discharge in an argon/oxygen gas mixture with a cobalt target Plasma Sources Sci. T. 28 (2019) 115020(1) - 115020(13).

3)* R. Hippler, M. Čada, V. Straňák, C. A. Helm, Z. Hubička Pressure dependence of singly and doubly charged ion formation in a HiPIMS discharge J. Appl. Phys. 125 (2019) 013301(1) - 013301(7).

4) M. Zanáška, Z. Turek, Z. Hubička, M. Čada, P. Kudrna, M. Tichý, Floating harmonic probe for diagnostic of pulsed discharges, Surface & Coatings Technology 357 (2019) 879–885.

5)* H. Hajihoseini, M. Čada, Z. Hubička, S. Ünaldi, M. A. Raadu, N. Brenning, J. T. Gudmundsson, D. Lundin, The Effect of Magnetic Field Strength and Geometry on the Deposition Rate and Ionized Flux Fraction in the HiPIMS Discharge, Plasma 2 (2019) 201 - 221.

* International collaboration

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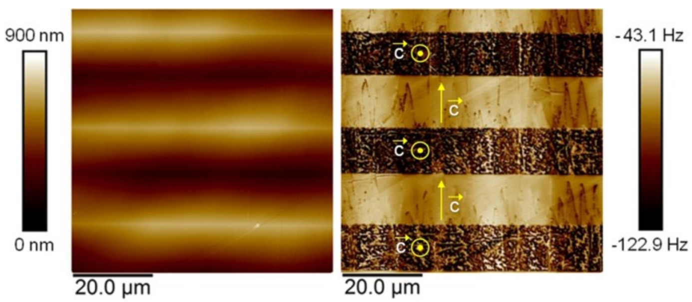
## RA3 - Plasma methods of preparation of thin metallic and intermetallic layers (J. Lančok)

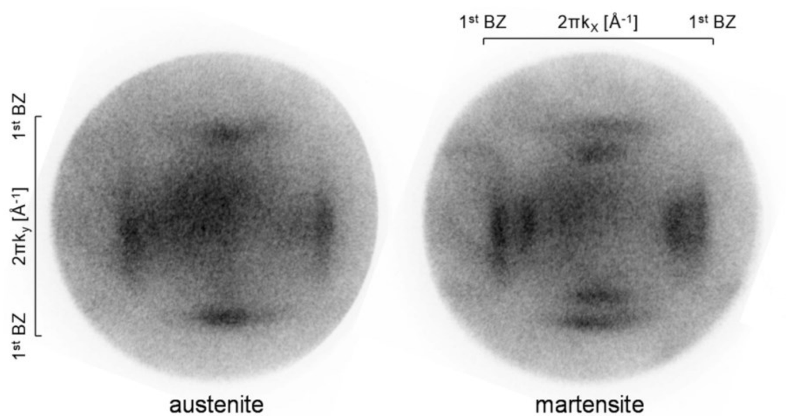
The research activity is divided into two parts:

- **Characterisation of the electronic structures of Heusler alloys in cooperation with VP1.**
- Fabrication of Heusler alloys with outstanding magnetic and magnetooptic properties

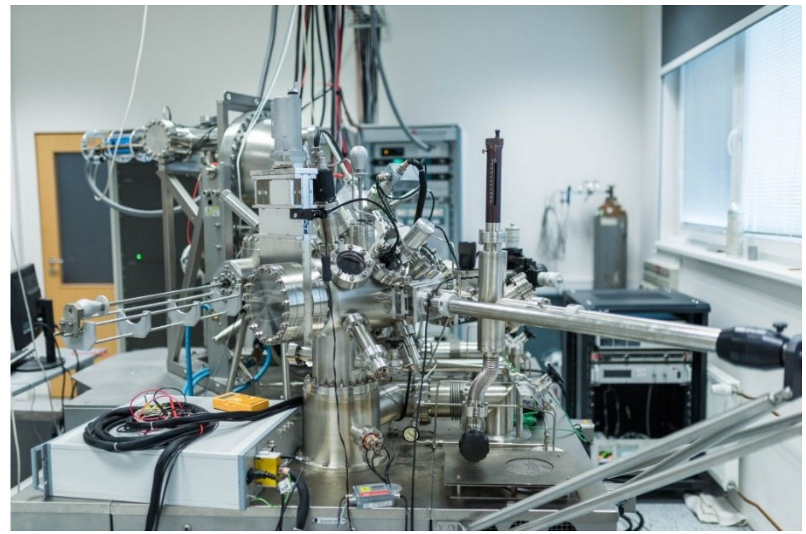
The electronic structure and twinning in the martensitic phase of Ni-Mn-Ga Heusler alloy determined by theory and experiment was studied and published in PRB.




AFM/MFM images of the Ni2MnGa (001)




PEEM images of an equi-energetic cut at *EF*



A NanoESCA photoemission spectrometer (Scienta Omicron) based on a PEEM column and a double-hemispherical-imaging energy filtering. This system we used for structural and chemical analyses in many RA.

*O. Heczko, V. Drchal, S. Cichoň, L. Fekete, J. Kudrnovský, I. Kratochvílová, J. Lančok, V. Cháb, Phys. Rev. B 98 (2018) 184407.*

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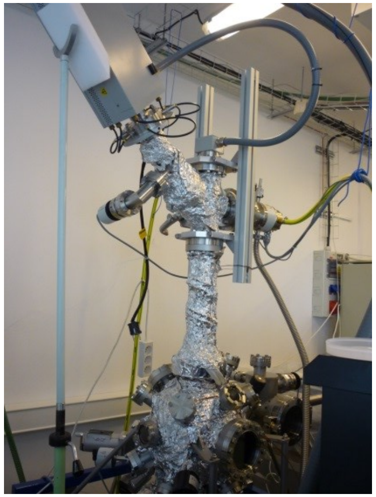
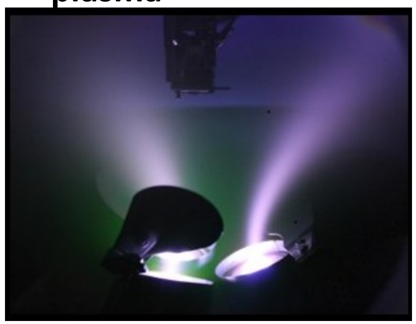
# RA3 - Plasma methods of preparation of thin metallic and intermetallic layers (J. Lančok)

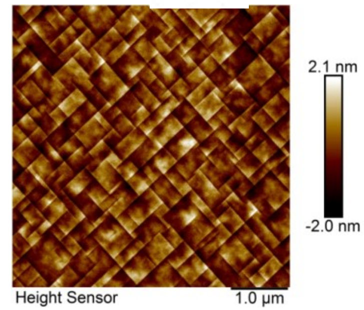
- **Fabrication of Heusler alloys with outstanding magnetic and magnetooptic properties**

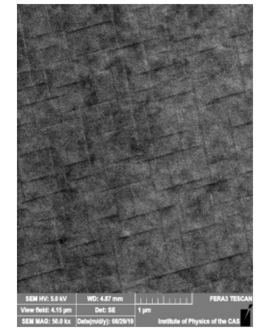


- **UHV deposition chamber for magnetron sputtering**
- **Mass spectroscopy of plasma**



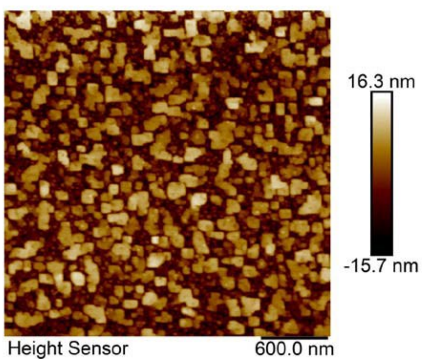
## $Rh_2MnSb$



- epitaxial smooth tetragonal HA $Rh_2MnSb$ with Tc=210 K.
- changing the DC power - inverse HA $Mn_2RhSb$ with Tc=290 K and ferromagnetic cubic RhMnSb with Tc=290 K were fabricated

## $Rh_2MnBi$ – not successful




epitaxial growth of $Rh_2Mn_5Bi_4$ alloy high purity and a Heusler-like behavior.

- Tc=270 K
- Magnetization 20-50 emu/g

*S. Cichoň ,Heusler-like Rh2Mn5Bi4 thin film alloy epitaxially grown on MgO(001) Submited to TSF*

## $Co_2TiZ$ ; Z=Al,Si,Ge,Sn

- Fabrication of Weyl semimetals containing Weyl nodes for extraordinary magnetooptics properties
- New GAČR project with MFF UK

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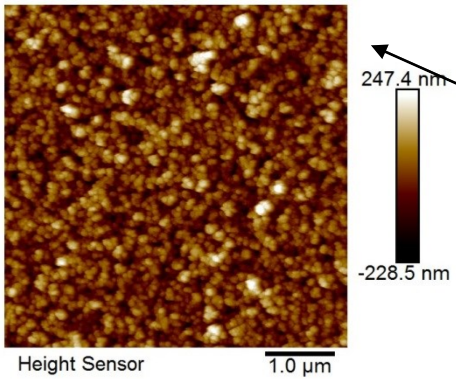
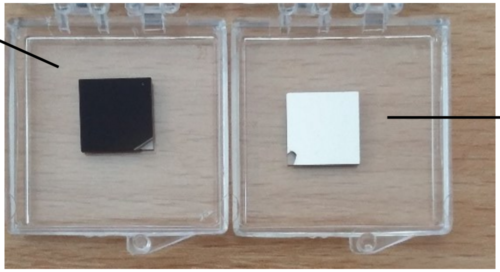
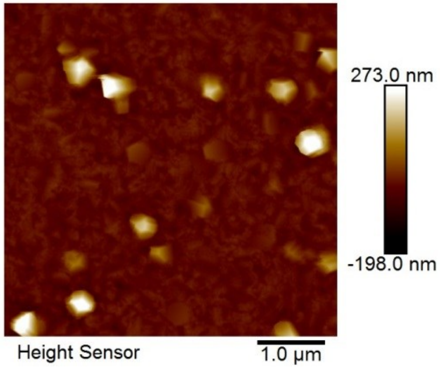
# RA4 - Thin-film chemical sensors (M. Novotný)

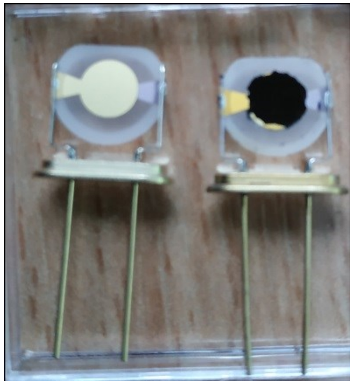
Black aluminium films growth by magnetron sputtering :***light absorber for pyroelectric energy harvesting***
***layers for QCM chemical sensors***



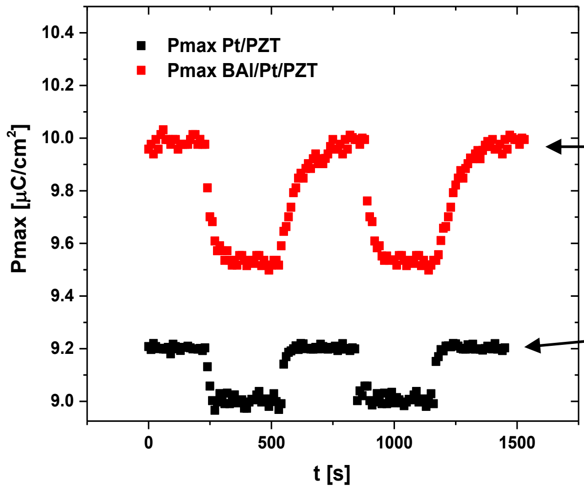



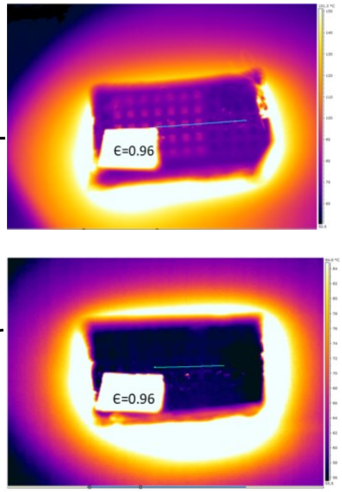
**The crucial parameter is presence of nitrogen during sputtering**



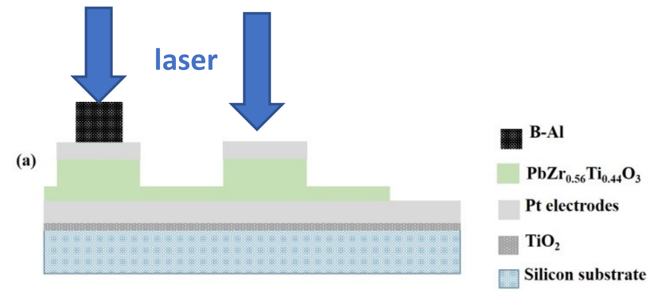
## Pyroelectric voltage measurements

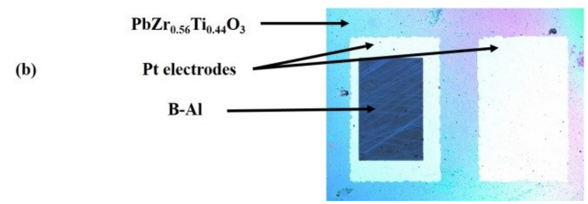



**Thermovision of surfaces**

***JAP 126 (2019) 214501***





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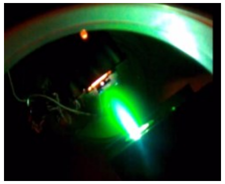
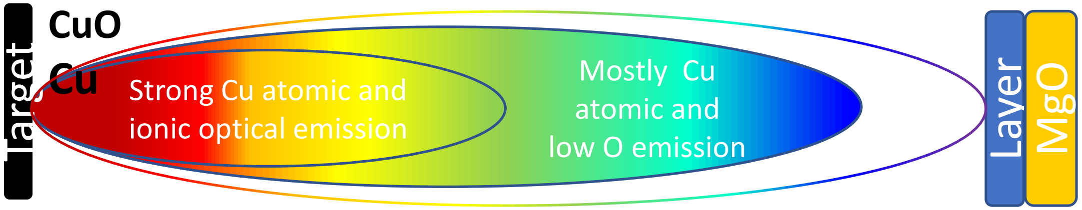
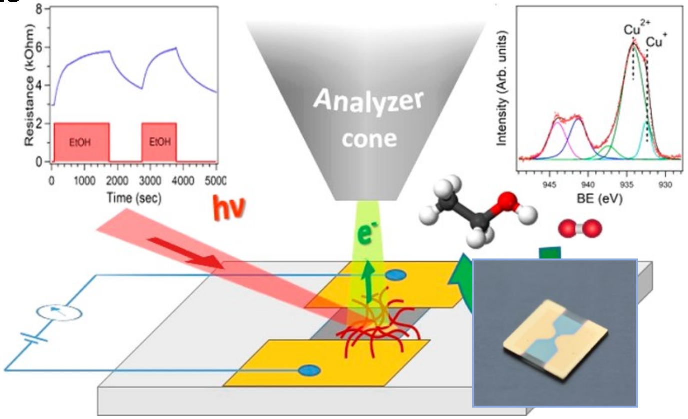
# **RA4** - Thin-film chemical sensors (M. Novotný)

## By Pulsed Laser Depositon ultrathin epitaxial $Cu_2O$ films

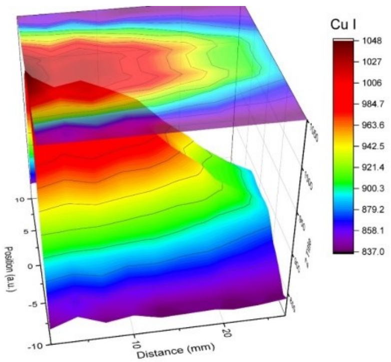


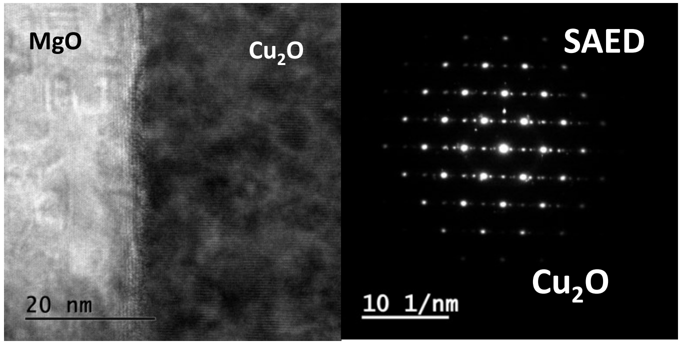
**Highly sensitive electrochemical gas sensors based on inorganic materials**

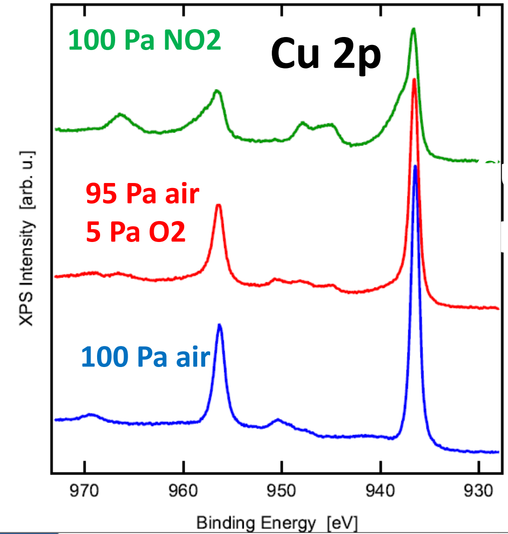


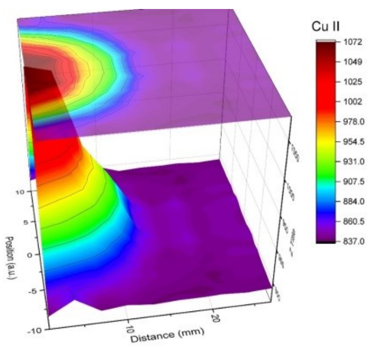




*J. Phys. Chem. C 2019, 123, 29739−29749*




- (110) epitaxial $Cu_2O$ films were fabricated on (100) MgO substrate at temperature above 600 °C and oxygen pressu in the range $10^{-2}$-$10^{-3}$ Pa
- Optical gap 2.3 eV
- P-type semiconductor

***Will be presented at E-MRS 2020***

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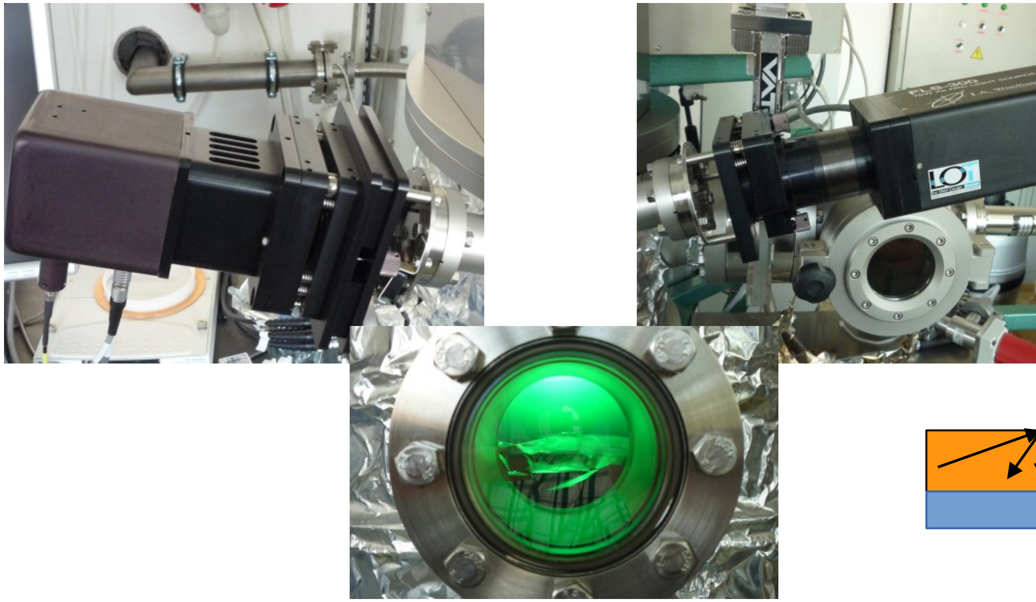
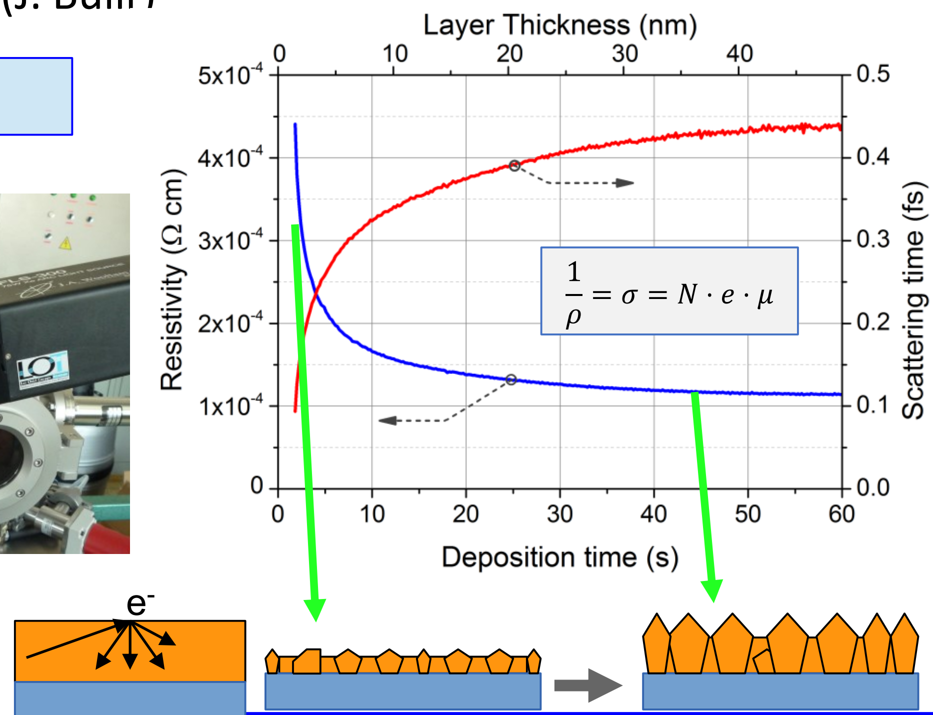
# **RA5** – Optical materials-plasmon structures (J. Bulíř)

- Ellipsometer: J.A.Woollam, M2000






Group IVb transition metal nitrides (TiN, ZrN, HfN) are premising material for plasmonic applications:

- Optical properties
- Technological aspects of fabrication
- Mechanical properties - hardness, wear resistance, adhesion

In-situ spectral ellipsometry is powerful technique to monitored the growing films

- The decrease of the electrical resistivity is associated with the free-electron scattering
- **Fine crystallites** at the beginning of the growth – enhanced probability of electron scattering at grain boundaries
- Growth of **grain size** during the deposition process – decrease of electron scattering at grain boundaries
- Free-electron scattering at **layer interfaces** – thickness dependence

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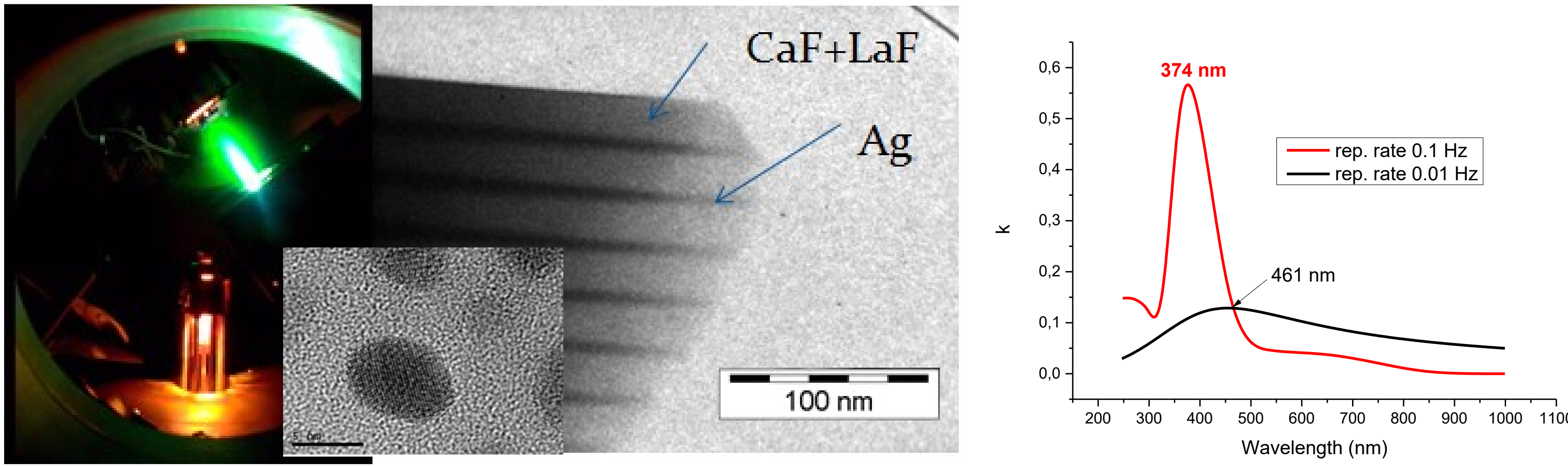
## **RA5** – Optical materials-plasmon structures (J. Bulíř)

**Fabrication of metal nanoparticles embedded in fluoride thin films for luminescence and magnetooptic applications by hybrid Pulsed Laser Deposition and Elecron beam evaporation**




*Fabrication of Ag NPs by using PLD embedded in $LaF_3$+$CaF_2$ matrix fabricated by EBE-left. Cross section of the layered Ag NPs (right) and HRTEM. Right the ex-situ ellipsometry of films fabricated at different laser rep. rate*

- enhance luminescence properties of $RE^{3+}$ ions is using **plasmonic behaviour** of **metallic nanoparticles**
- The fluoride materials appropriately doped by RE ions ($Pr^{3+}$, $Ce^{3+}$, $Nd^{3+}$) ions are promising for tuneable **UV up-conversion** as well as **down-conversion**
- Magnetooptic materials – large Faraday rotation and low absorption – only few materials.
- approach to combine MO materials with plasmonic nanostructures. By an adequate internal, the magneto-optical activity of these systems can be greatly increased due to the electromagnetic field enhancement associated with the plasmon resonance. Simultaneously, the magnetic functionality permits the control of the plasmonic properties by an external magnetic field, which allows the development of active plasmonic devices. ¨- ***new GAČR project – presentation on E-MRS 2020***

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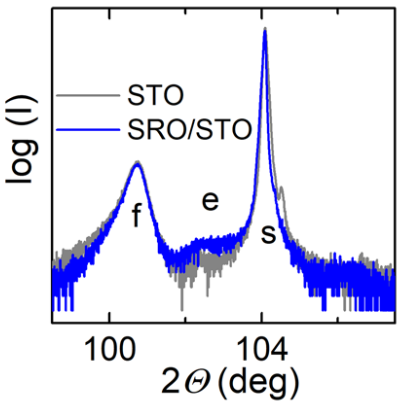
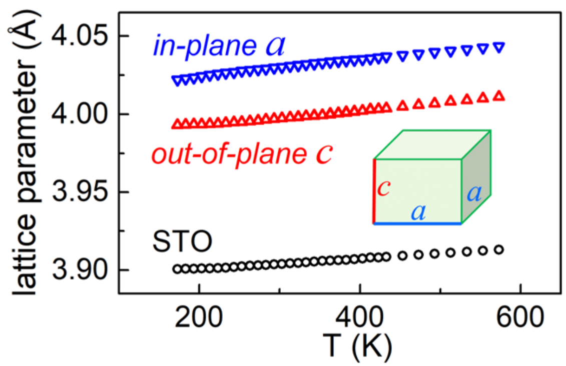
## **RA6** – Structures exhibiting a combination of ferromagnetic properties (M. Tjunina)

**Fabrication of epitaxial perovskite oxide films by Pulsed Laser Deposition and tailored properties by defect and by thermal strain.**

### $BaTiO_3$ on $SrRuO_3$/STO – thermal strain



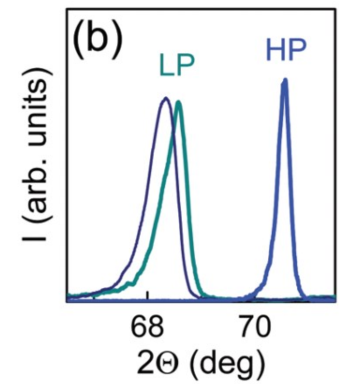




Details of the Θ-2Θ scans around the (004) perovskite diffraction peaks in the 100-nm-thick BTO films on STO and SRO-coated STO-left. Right -lattice parameters as a function of temperature in the BTO film on STO

- thermal tension forming during cooling from a high synthesis temperature results in the in-plane orientation of ferroelectric polarization.
- Owing to the in-plane polarization and the electric-field-induced polarization rotation, bottom-to-top $BaTiO_3$ capacitors exhibit excellent performance
- we anticipate that thermal strain can effectively tune the performance of many materials.

***M. Tyunina, O. Pacherova, J. Peräntie, M. Savinov, M. Jelinek, H. Jantunen, A. Dejneka, Sci. Rep. 9 (2019) 3677 - 3684***

### $BaTiO_3$ /STO – oxygen vacancies




Θ–2Θ scan around (003) perovskite diffraction in the low-pressure (marked by LP) and high-pressure (marked by HP) films.

- oxygen-vacancy-related defects are studied in a broad spectral range of 0.75–8.8 eV.
- the defects produce in-gap states and internal
- electric field, which are manifested by an additional optical
- transition below the gap and significant blueshifts of the interband transitions, correspondingly.

***Tyunina, D. Chvostova, A. Dejneka, Phys. Chem.Phys. 21(2019) 7874***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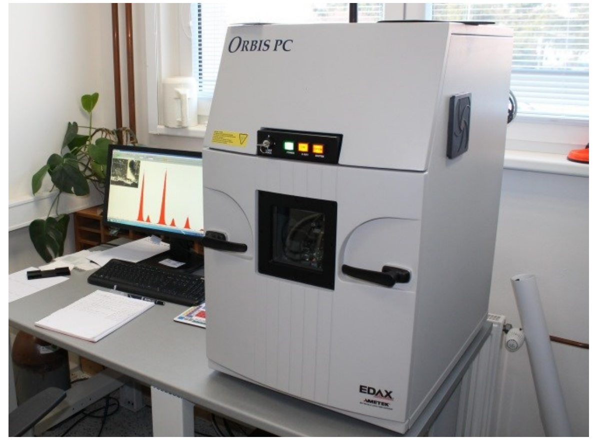
# Experimental facilities

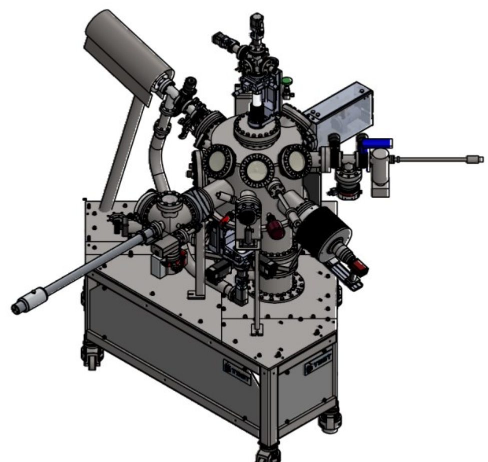
**Spectral Ellipsometry**
monitoring of the deposition process
at operation from Jully 2019




**XRF**
Spectrometer with focused polycapillary for thin film composition installed in December 2019


**Ion mass spectrometer EQP**
Spectrometer with LG probe can analyze plasma parameters October 2019

**Laser-MBE** system for PLD with high pressure RHEED for RA3,4,5 and 6 will be installed in the new building spring 2021



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# Summary of the main goals of RP5 for the following period (01/01/2020-30/06/2020)

We plan to finish the tender for the plasma system for the deposition of sulfide and selenides thin films.

Further goal is to complete the tender for Laser-MBE deposition system with integrated RHEED system for fabrication of epitaxial thin films.

The research will be oriented on the reactive HiPIMS system and the control of physical processes during the growth of semiconducting thin films. The physics of hybrid HiPIMS+ECWR plasma will be further investigated for very thin film multilayer structures. The physics of bipolar HiPIMS system will be investigated by very specific diagnostic tools like capacitive probe, ion mass analyser, RF planar probe.

The research will continue in the direction of thin films deposition with outstanding magnetic and magnetooptic properties using the method of DC magnetron sputtering from multiple targets in the UHV system. Epitaxial RhMnSb layers with tetragonal crystal structure as well as $Co_2TiSn$ were already prepared on MgO substrates and in cooperation with RP1, the magnetic properties of these materials will be studied.

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