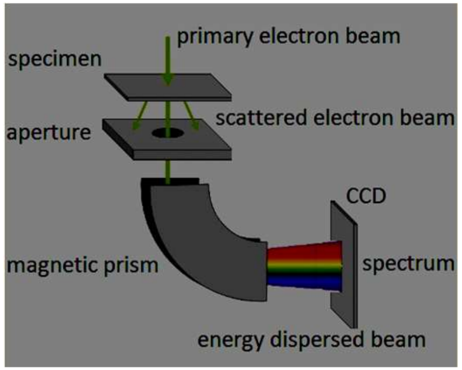
# Plasmon-Enhanced Terahertz EPR Microscopy

**BUT contribution**

Stuttgart, October 1 – 3, 2019

# Mapping plasmonic near fields – EELS (T1.3, M5-M18)




## Electron energy loss spectroscopy

- operation mode of transmission electron microscope
- **spatial resolution 1 nm**
- **spectral resolution ~ 0.15 eV**
- detection limit ~ 0.6 eV

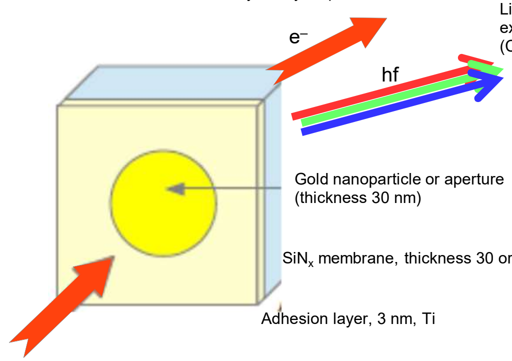
high-energy electrons (300 keV)

Only electric field is detected:

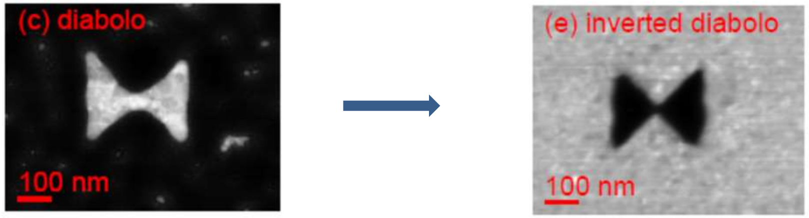
$$\Delta E = e \int dt\, \mathbf{v} \cdot \mathbf{E}^{\mathrm{ind}}[\mathbf{r}_e(t), t] = \int_0^{\infty} \hbar\omega \, d\omega \, \Gamma_{\mathrm{EELS}}(\omega)$$

$$\Gamma_{\mathrm{EELS}}(\omega) = \frac{e}{\pi\hbar\omega} \int dt \, \mathrm{Re}\{e^{-i\omega t} \mathbf{v} \cdot \mathbf{E}^{\mathrm{ind}}[\mathbf{r}_e(t), \omega]\}$$

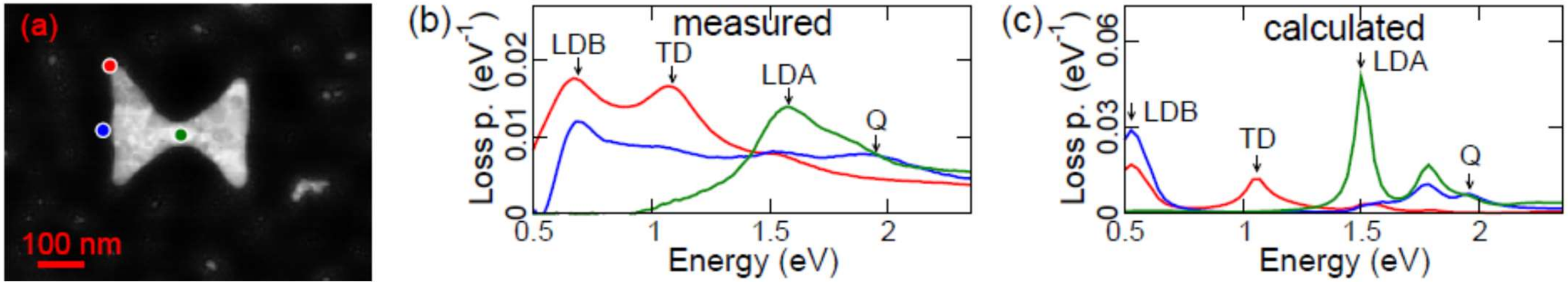
García de Abajo, Rev. Mod. Phys. **82**, 209 (2010)




Magnetic field distribution (qualitative): Babinet's principle



# EELS maps for diabolo antennas (T1.3, M5-M18)

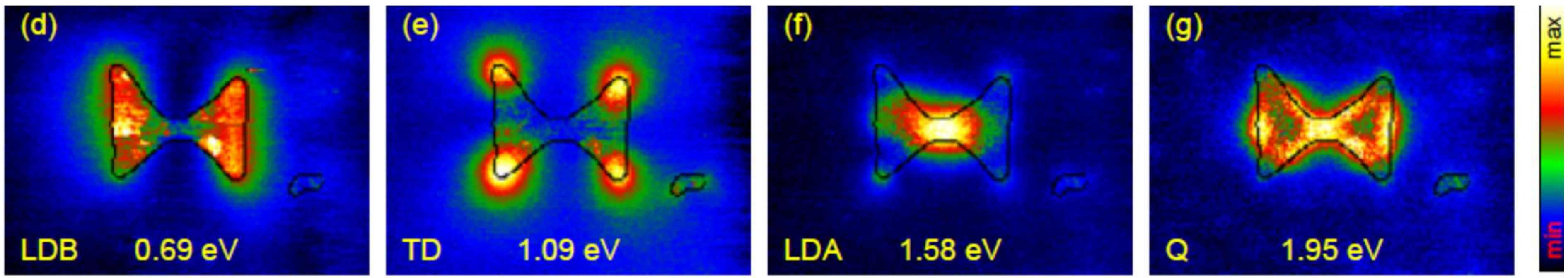



LDB – Longitudinal-Dipolar Bonding mode

TD – Translational-dipolar mode

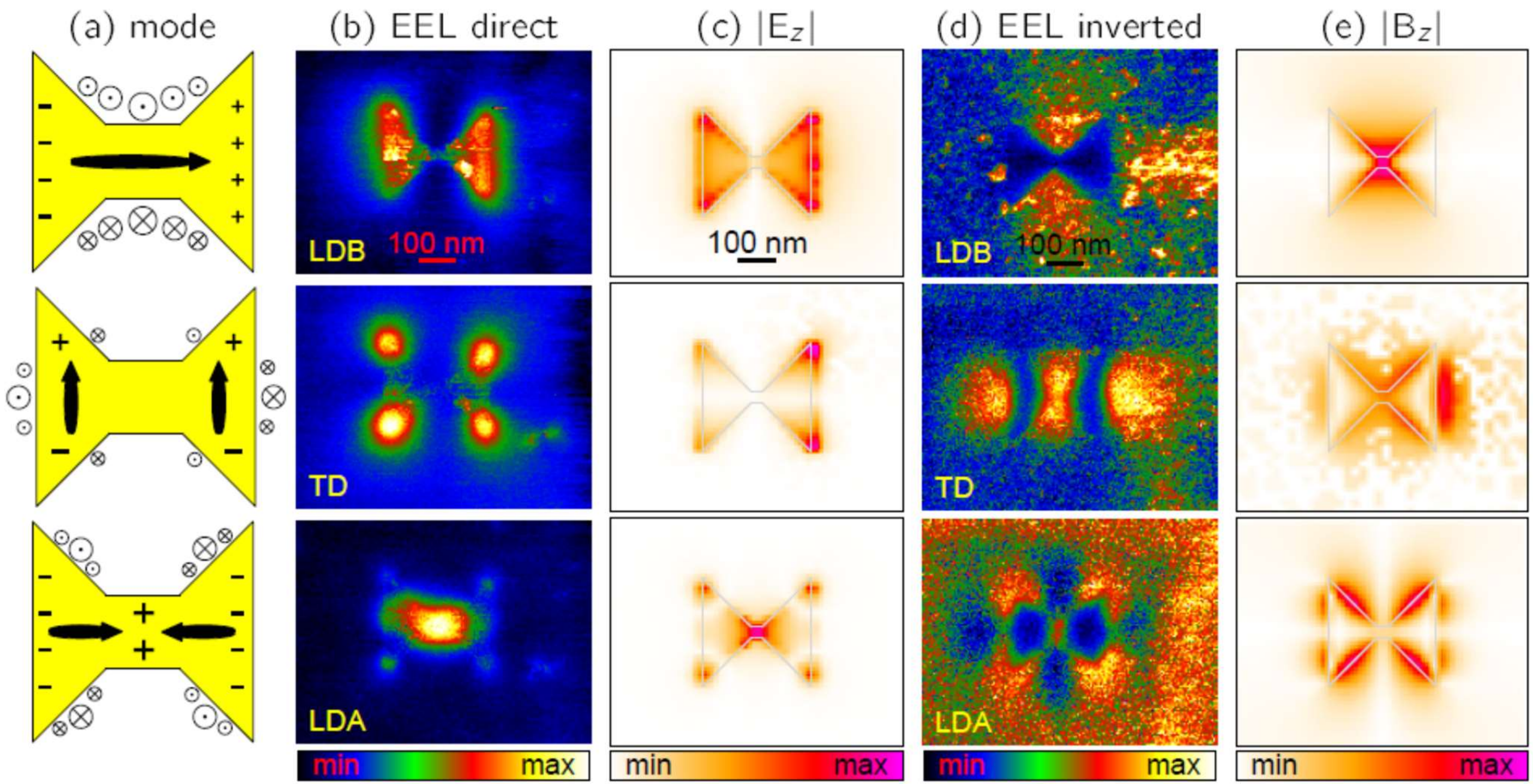
LDA – Longitudinal-dipolar antibonding mode

Q – Quadrupolar-hexapolar mode




Křápek et al.,, arXiv 1905.09210 (2019).

# EELS maps for diabolo antennas (T1.3, M5-M18)




Křápek et al, arXiv 1905.09210 (2019).

# T1.4 (M8-M30)



## Sample preparation for PE THz EPR spectroscopy (Deliverable 1.5)

1. Evaporation of copper(II)phthalocyanines
2. Deposition of larger molecules by *atomic layer injection* [1]
   (solution of molecules is injected trough a pulse valve into a vacuum chamber):

   **Nano-microscopic droplets** containing molecules are delivered to the substrate (without their decomposition).

We have tested the system on the following single molecule magnets (SMMs):

(1) [1,1'-Bis(diphenylphosphino)ferrocene]dibromocobalt(II) – [$CoBr_2$(dppf)]

(2) [1,1'-Bis (diphenylphosphino)ferrocene]dichlorocobalt(II) – [$CoCl_2$(dppf)]

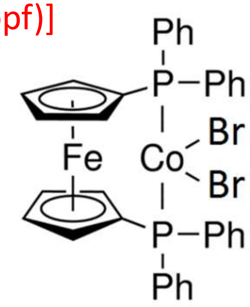
(3) bis(dibenzoylmethane) copper(II) – [$Cu(dbm)_2$]

[1] T. KRAJŇÁK: Deposition of large organic molecules at UHV conditions (in Czech). Diploma thesis, BUT 2019 (Supervisor: Jan Čechal)

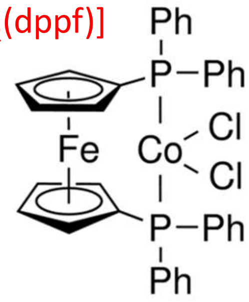
# T1.4 (M8-M30)

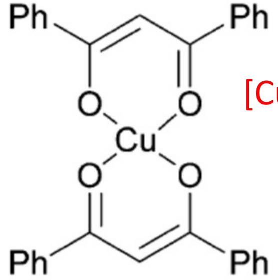
## Sample preparation for PE THz EPR spectroscopy (Deliverable 1.5)

[$CoBr_2$(dppf)]

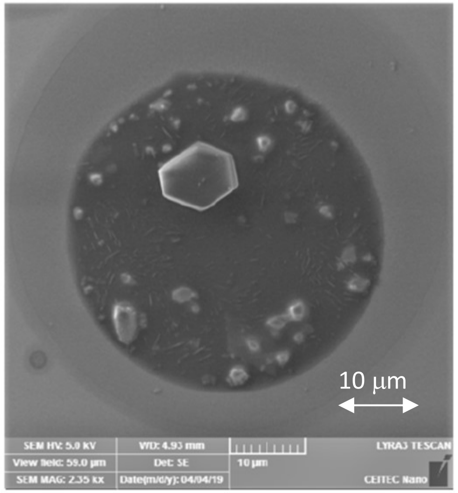


[$CoCl_2$(dppf)]





[$Cu(dbm)_2$]




[$CoCl_2$(dppf)] nano/microcrystals obtained by deposition on a gold surface from the 3 mM solution in chloroform (Field of view 60 micrometres.

a good candidate for PE EPR microscopy?

T. KRAJŇÁK, Diploma thesis, BUT 2019 (Supervisor: Jan Čechal)

# WP1 – PE THz EPR spectroscopy



## Proof of concept of PE EPR effect

**What should be done:**

1. Finding antennas with optimal resonances:
   - Measurement of the already fabricated antennas (USTUTT, NanoGune?)
   - Fabrication of optimal antennas (NanoGune, BUT)
   - Simulation of antennas beyond the diabolo concept (split-ring resonators, swiss rolles,...) – comparisson of their performance with respect to diabiolo ones (BUT)

When?: asap

- Attempt to fabricate a field of *pyramidal antennas* on a Si surface (BUT, *deadline: XII/2019*)

# WP1 – PE THz EPR spectroscopy



## Proof of concept of PE EPR effect

**What should be done:**

2. PE EPR response:
   - Measurement on optimized antennas covered with a *BDPA radical* (?), 4 K, B > 0T – *present apparatus* (USTUTT, XII/2019) – *in progress*
   - Measurement on optimized antennas covered with *a BDPA radical* (?), 4 K, B > 0T – *new optimized apparatus* (USTUTT, III/2020), *available from: ????*
   - Preparation of samples with new EPR active materials (phthalocyanines, …..) and antennas (BUT, USTUTT, XII/2019) ➡ PE EPR experiment (USTUTT)

**Optionally:**

- Fabrication of an alternative EPR active material for measurements at RT and zero magnetic field (NanoGune, BUT) – *YFeO3 thin films (sol-gel, PLD using pallets)?*
- Measurement on the alternative materials (RT, zero magn. field) provided with antennas (NanoGune)

# WP2 – PE THz EPR microscopy



## Platform for PE THz EPR - Assembling and Testing

**What should be done:**

1. Fabrication of cantilever tips for PE EPR microscopy (NanoGune, BUT, *deadline: XII/2019*)
2. Instalation of the SPM unit into the Platform for PE EPR microscopy (BUT, *deadline: II/2020*)
3. Platform ready for Proof-of-Principle of PE THz EPR microscopy (USTUTT, deadline: *II/2020*)

   Note: BUT master's student trained for SPM operation at USTUTT from II/2020

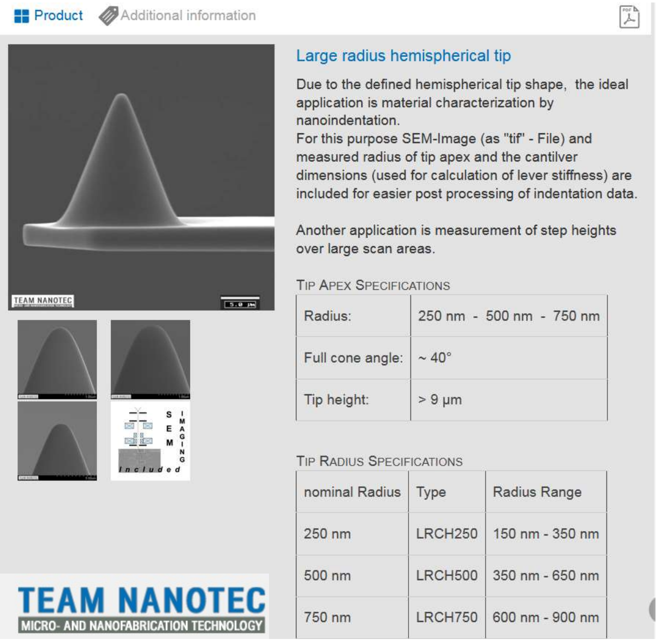
4. Optimized cantilever tips for PE EPR microscopy (USTUTT, deadline: *VI/2020*)
5. Preparation of samples - patterned thin films, [CoCl2(dppf)] nano/microcrystals,.... (USTUTT, BUT, deadline: *II/2020*)

# T2.2 (M12-M30)



## Fabrication of cantilevered THz antenna tips

- Diabolo antennas can be easily fabricated by focused ion beam milling of gold coated commercial atomic force microscopy tips
- Tip height < 20 µm, thus suitable only for illumination frequency > 1 THz


Product | Additional information

**Large radius hemispherical tip**

Due to the defined hemispherical tip shape, the ideal application is material characterization by nanoindentation.
For this purpose SEM-Image (as "tif" - File) and measured radius of tip apex and the cantilver dimensions (used for calculation of lever stiffness) are included for easier post processing of indentation data.

Another application is measurement of step heights over large scan areas.

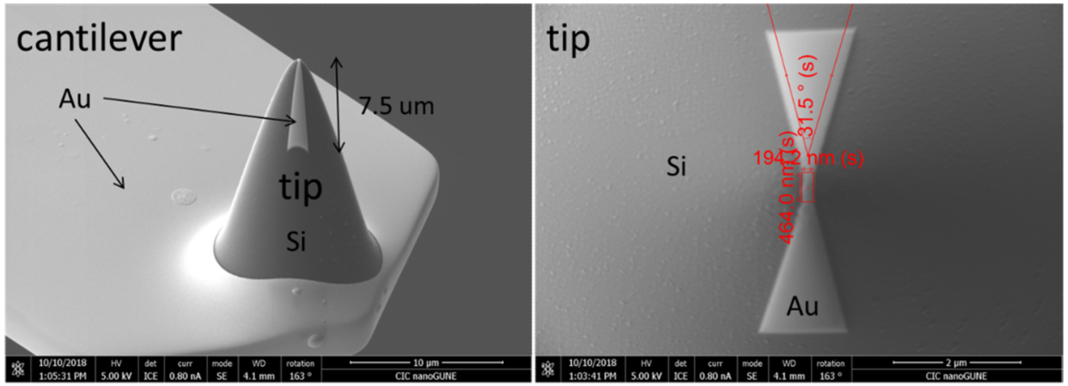
TIP APEX SPECIFICATIONS

| | |
|---|---|
| Radius: | 250 nm - 500 nm - 750 nm |
| Full cone angle: | ~ 40° |
| Tip height: | > 9 µm |

TIP RADIUS SPECIFICATIONS

| nominal Radius | Type | Radius Range |
|---|---|---|
| 250 nm | LRCH250 | 150 nm - 350 nm |
| 500 nm | LRCH500 | 350 nm - 650 nm |
| 750 nm | LRCH750 | 600 nm - 900 nm |

TEAM NANOTEC
MICRO- AND NANOFABRICATION TECHNOLOGY

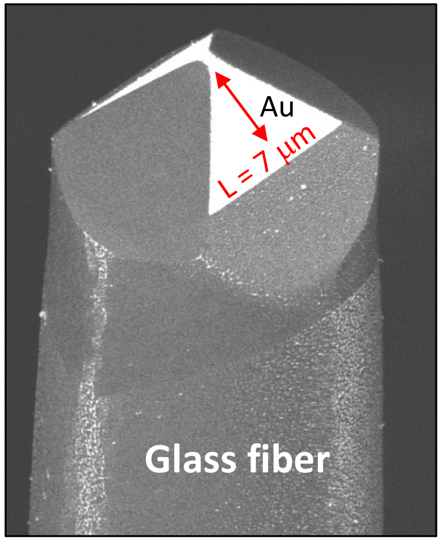


# T2.2 (M12-M30)

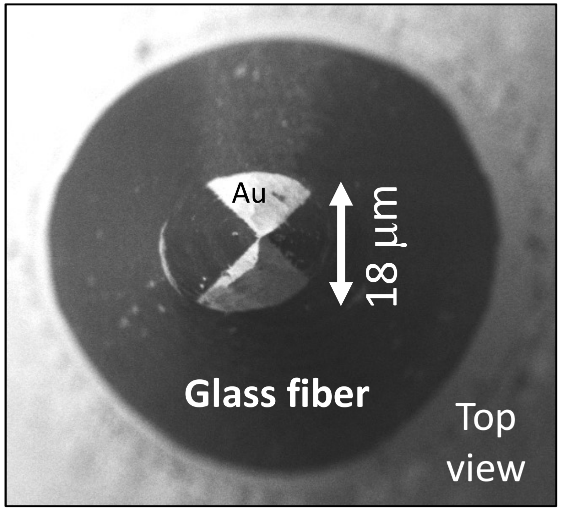
## Fabrication of THz antennas on FIB sharpened glass fibres

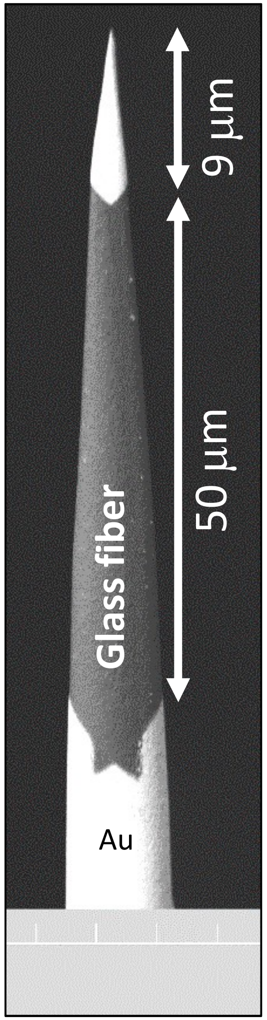
- FIB can be used for fabricating pyramidal and conical tips at the end of long glass fibres
- Antenna length L can be 100 μm, thus suitable for 300 to 600 GHz illumination

Pyramidal glass fiber probes




Conical glass fiber probes



# T2.2 (M12-M30)



## Fabrication of THz antennas on FIB sharpened glass fibres

- Tip must be transferred to the SPM probe
  - Manually
    - Suitable only for longer fiber-glass tips
    - Only on large probes – Tuning fork
  - Nanomanipulation in SEM
    - Suitable for any tip/probe combination
    - FIB cutting, FEBID/FIBID "welding"
    - Procedure like a TEM lamella preparation