Deposition of Molecular Magnets by Atomic Layer Injection

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Introduction

We present initial results on deposition of single-molecule magnets (SMM) employing Atomic Layer Injection (ALI) technique. ALI enables to deposit molecular layer from solution on samples under ultra-high vacuum (UHV) conditions. In this technique, the molecular solution is placed in the device, mixed with Ar gas and injected into UHV as microdroplets employing pulse valve. In this way a variety of molecules incompatible with thermal deposition can be placed on desired surfaces. We have employed X-ray photoelectron spectroscopy (XPS) to assess chemical composition of deposited SMM and found set of condition at which these SMM can be deposited intact. We found that, in general, this technique is capable of deposition of SMM in form of nano-microcrystals that precipitated from droplet of solution during its evaporation in UHV. Further research will be focused on reaching the homogenous deposition.

Materials and Methods

- Ultra-High Vacuum (base pressure 2×10^{-7} Pa)
- Sample at room temperature
- In-situ (XPS) and ex-situ (XPS, SEM) analysis

Substrates

- Si(111) with and without oxide layer
- 50 nm Au layer/Si(100) substrates

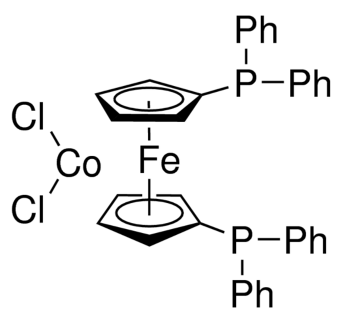
Solvents

- Dichloromethane CH_2Cl_2
- Chloroform $CHCl_3$
- Dimethylformamide $HCON(CH_3)_2$

Operation parameters

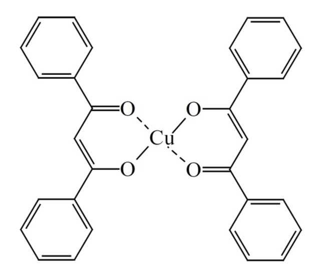
- Carrier gas pressure 300 - 840 mbar
- Pulse duration 5 – 20 µs
- Number of pulses

Tested Molecules



[1,1'-Bis(diphenylphosphino)ferrocene]dichlorocobalt(II) - DM18N

Field induced single-molecular magnet



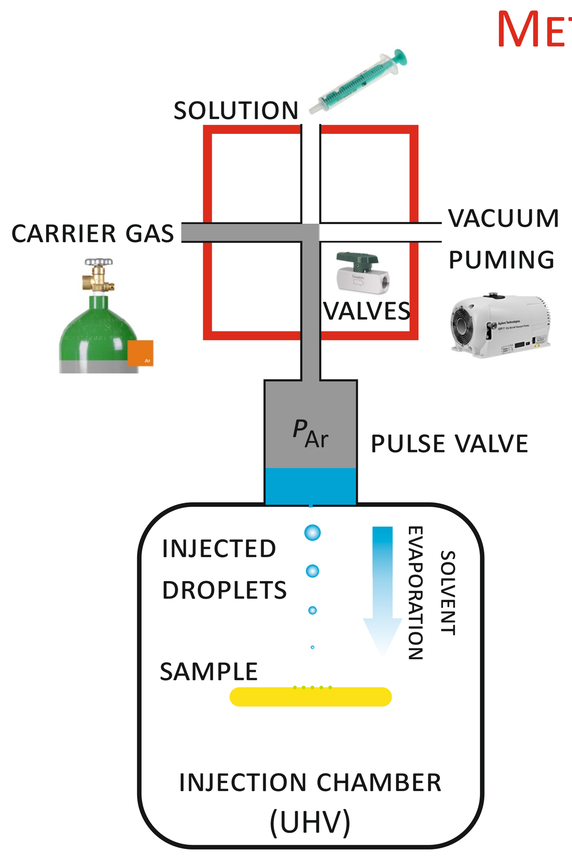
copper(II)dibenzoylmethane [Cu(dbm)₂]

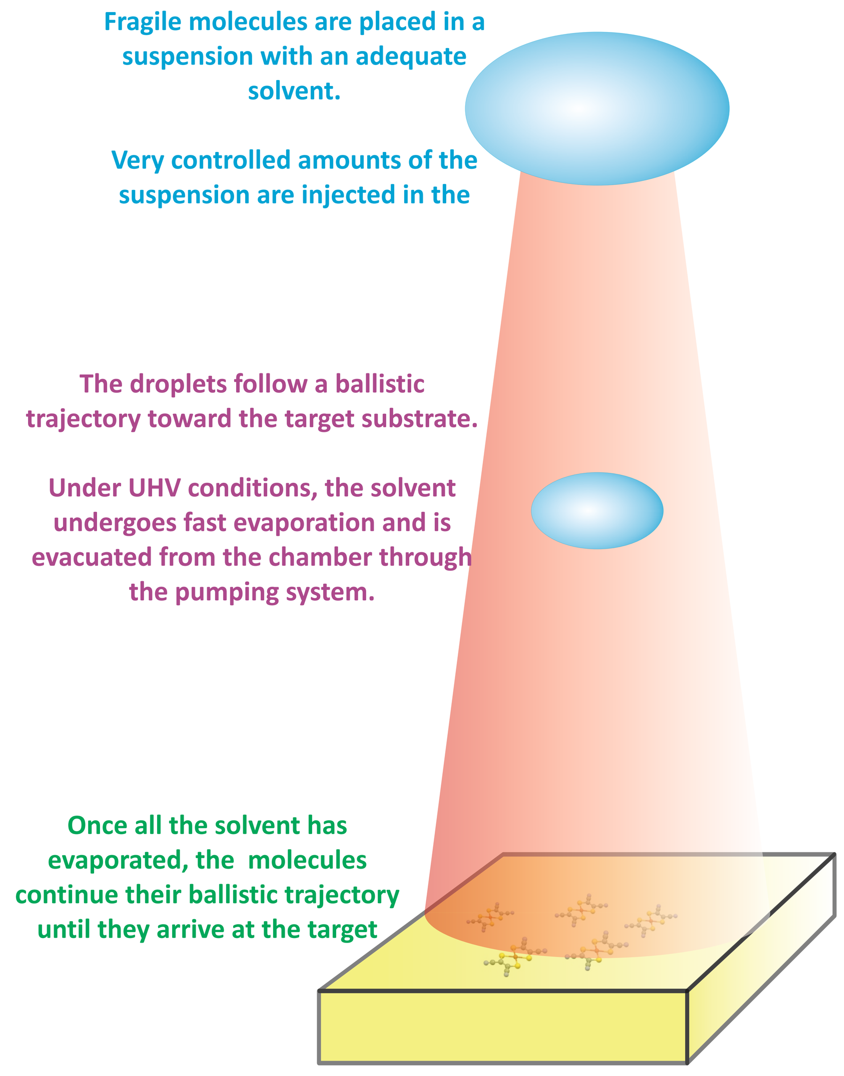
Molecular qubit

Atomic Layer Injection (ALI)

- Deposition of a range of materials (molecules, nanoparticles, nanotubes) from solution or colloidal suspension from solution onto sample in UHV.
- Suitable also for large or fragile molecules that degrade when heated.

Method Description

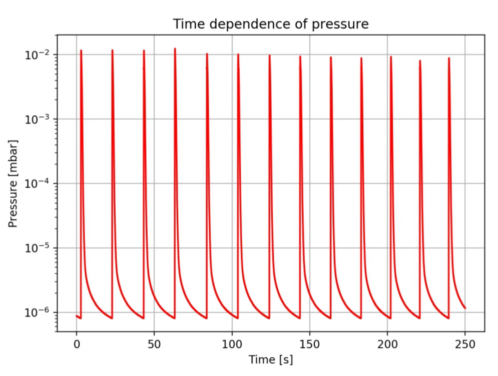




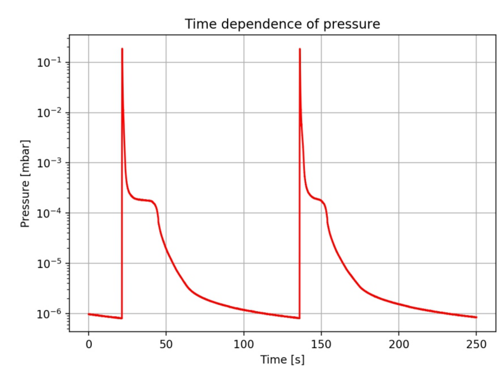
Deposition Results

Solvent Injection

Sequence of the individual pulses



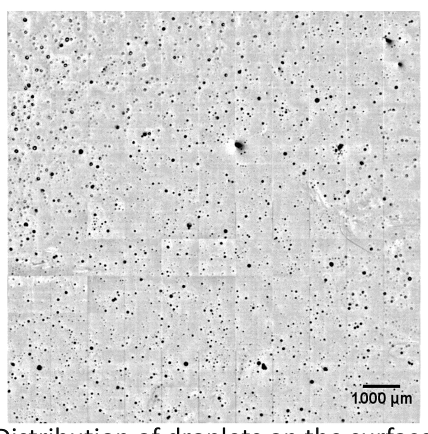
Chloroform: an easy recovery of base pressure



Dimethylformamide: quite difficult pumping

Droplet Formation

- The initial deposition geometry and parameters: deposition of droplets.
- Number and size distribution of droplets weakly depend on the pulse duration.
- Number of droplets increase with carrier gas pressure.

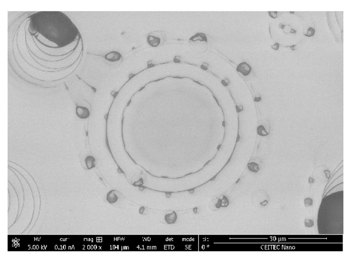


Distribution of droplets on the surface after pulse deposition of chloroform.

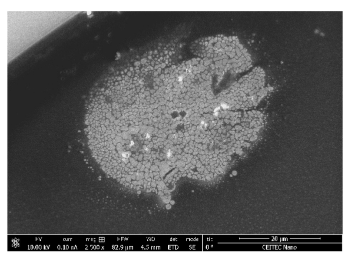
Molecular Deposition

- Formation of molecular nanocrystals within the area deposited droplets.

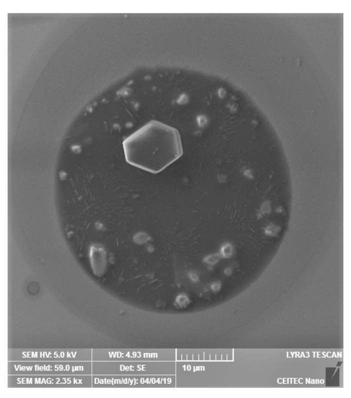
SEM analysis

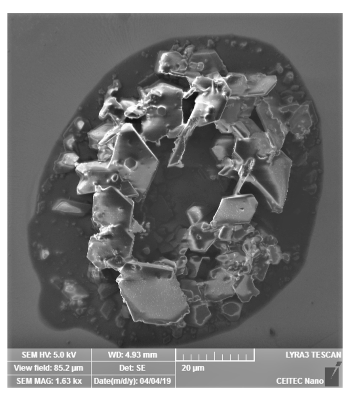


SEM on evaporated dichlormethane droplets on Au substrate



Crystallization of Cu(dbm)₂ deposited from 1 mM dimethylformamide solution

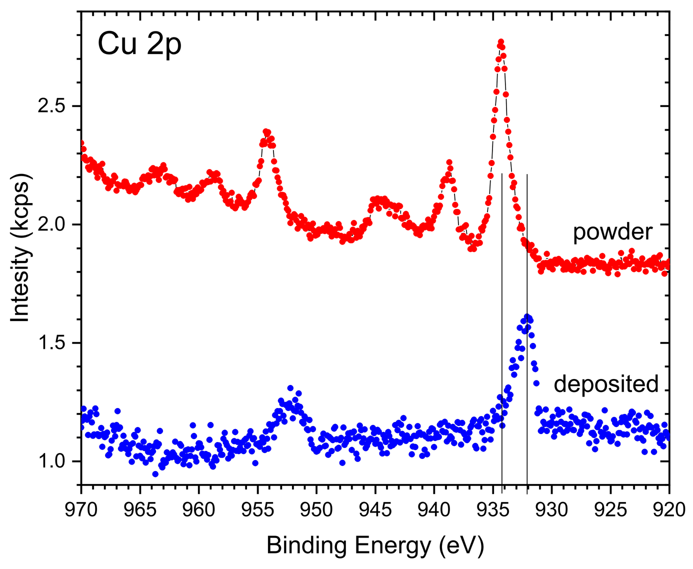




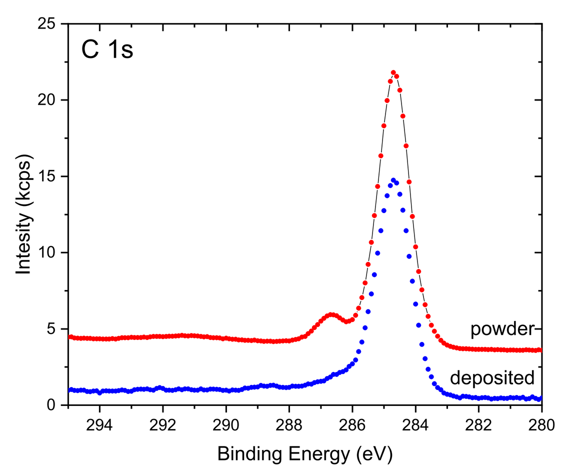
Crystalization of DM18N in the evaporating droplets deposited from 3 mM solution in chlorofom

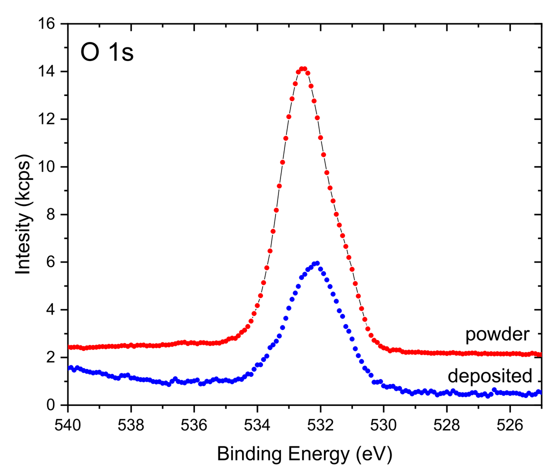
XPS analysis

- Ex-situ analysis - monochromatic Al Kα
- Cu(dbm)₂: all elements present in the XPS spectra.
- Different chemical state of Cu: $Cu^{2+} \rightarrow Cu^{1+}$ or Cu^{0}.
- DM18N lost $CoCl_2$ group at certain deposition conditions; Fe remained in the ferocene state.



XPS analysis of Cu(bdm)₂





ALI integration: in-situ UHV analysis

- Complex Ultra-High Vacuum (2×10^{-8} Pa)
- Combination of deposition and analysis

LEEM

- SPECS LEEM P90
- Imaging, micro-diffraction

STM

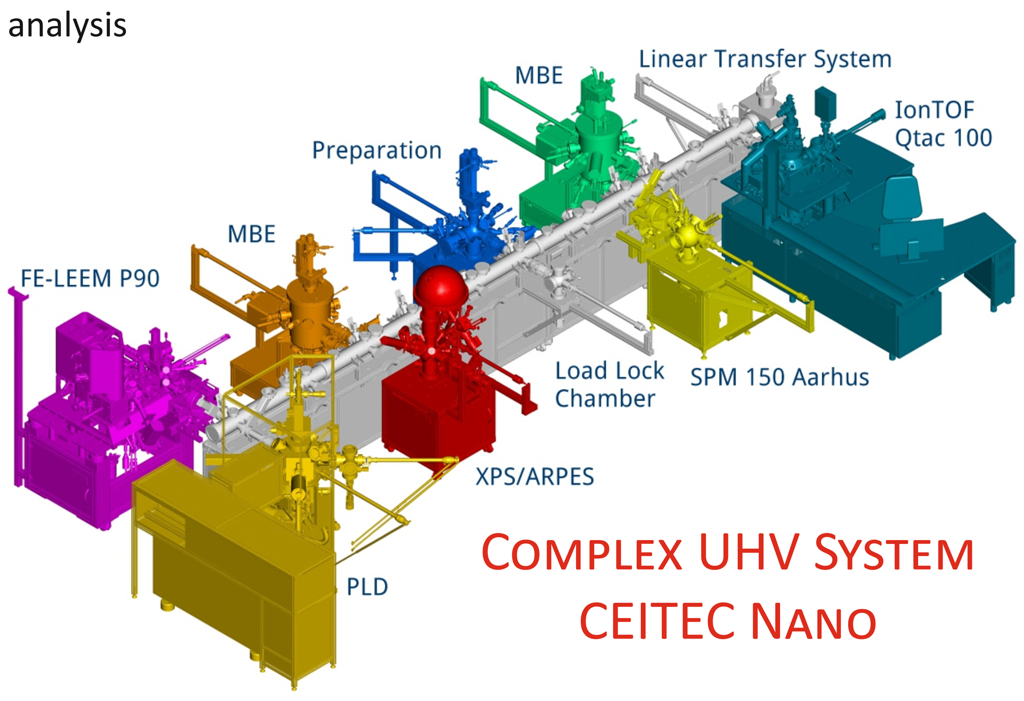
- SPECS Aarhus SPM
- Imaging at RT

XPS

- Non-monochromatic X-rays
- Sample cooled below 100 K

LEIS

- He, Ne, Ar ions
- Sensitivity to topmost layers



Complex UHV System CEITEC Nano

Conclusions

- Deposition of molecular nanomagnets and qubits from solution on sample in UHV.
- Both Cu(dbm)₂ and DM18N should be carefully deposited to present their chemical state
- Deposition of solvent droplets and their subsequent evaporation – formation of molecular nanocrystals on sample surface – to be prevented by further development.

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