Optimization of EBID nanowires

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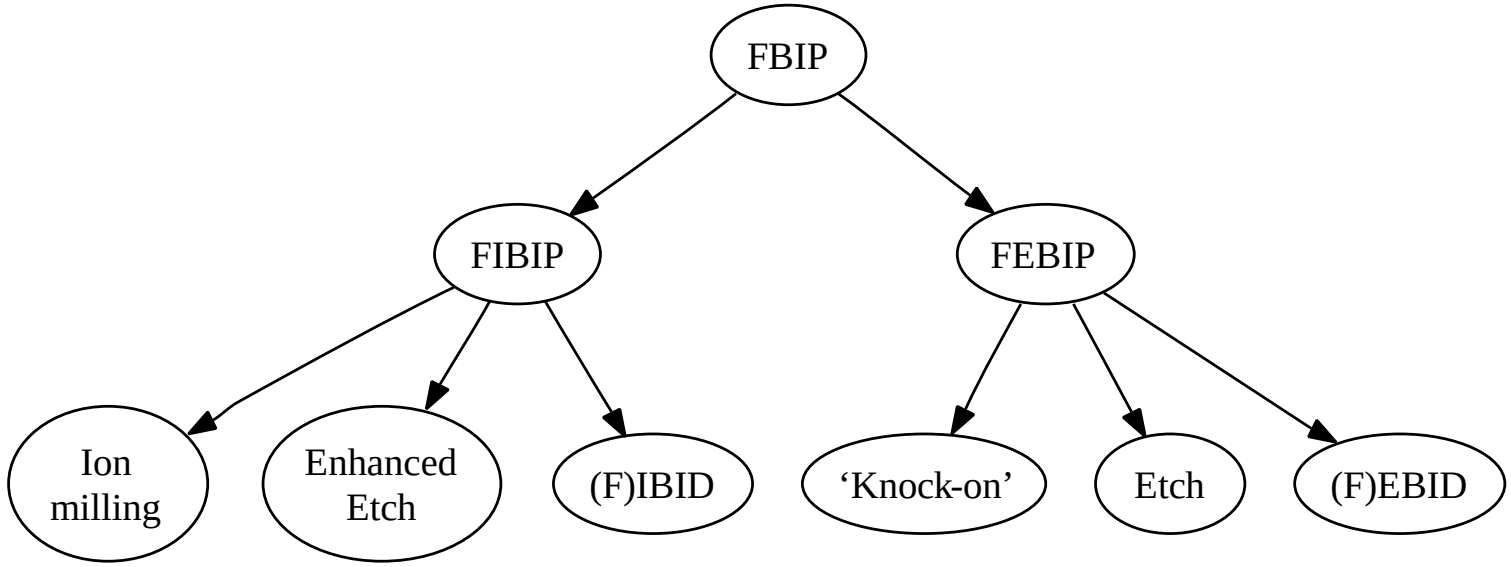
Overview

Topics:

- What is EBID
- Applications / possibilities
- State of the art
- Optimization and Project
- Experimental setup and techniques
- Experiments and (first) Results
- Conclusions

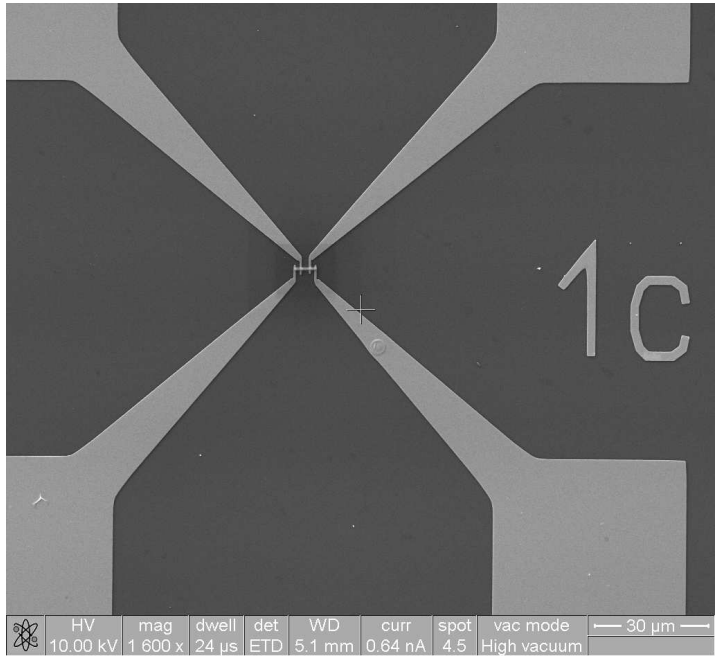
What is EBID

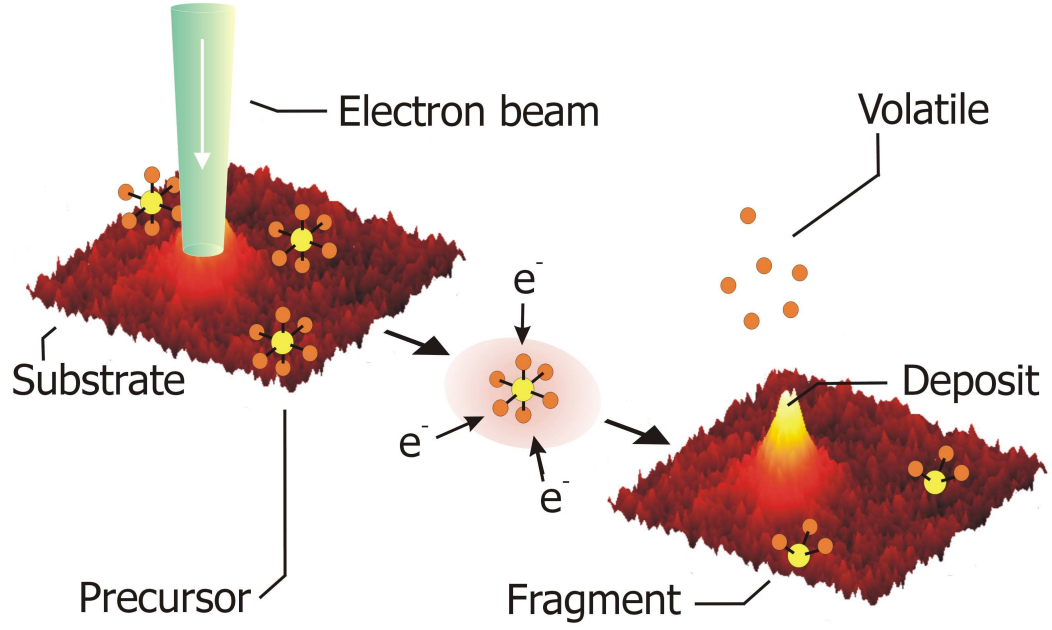
Direct Focussed Beam Process taxonomy:



- Similar processes for ion and electron beam
- Underlying mechanisms very different
- EBID: 1 nm patterns possible, process is a million times slower than EBL

What is EBID

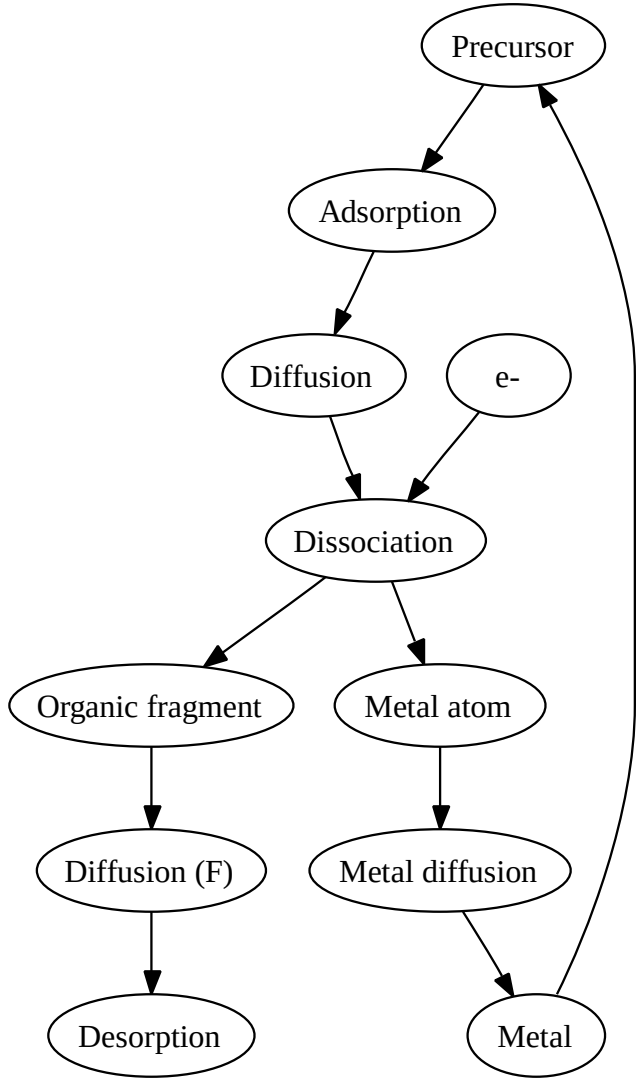




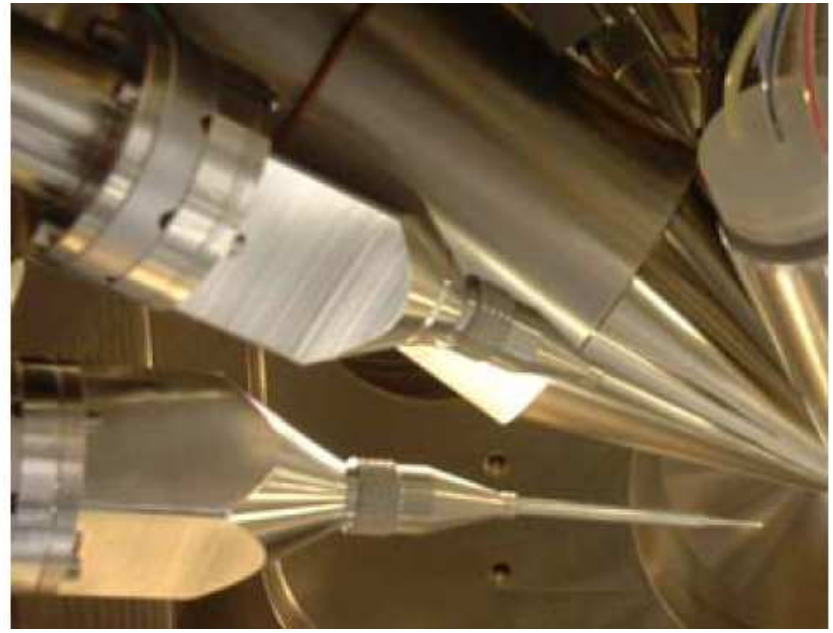
- C Contamination in SEM (known since 2 stage RP)
- 3D additive lithography with precursors
- Koops et al pioneered use of metallo-organic precursors to deposit 'metals'

How EBID is believed to work

by some, that is



GIS

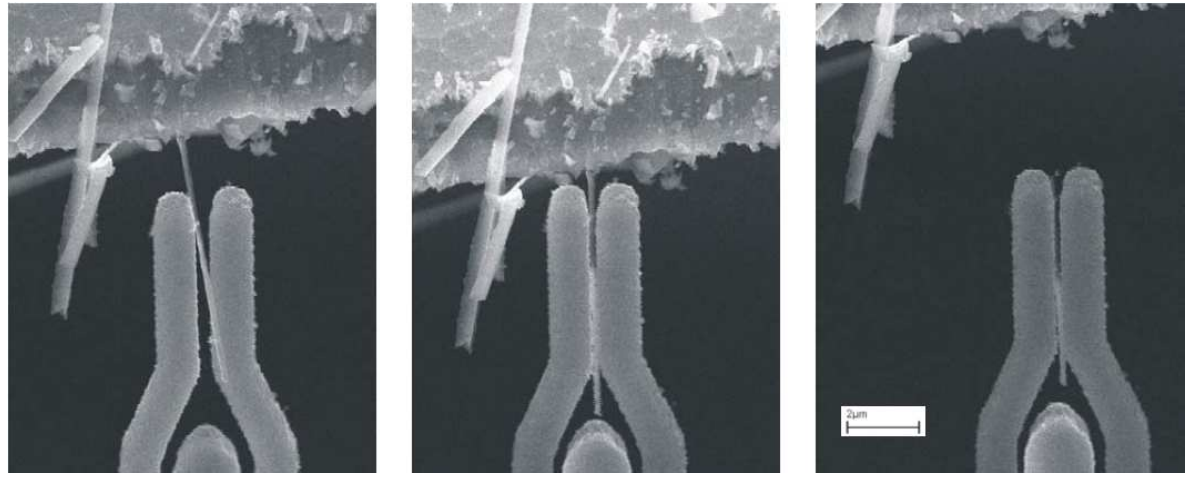


- Stainless steel 500 μm diameter needle
- pneumatic motion, 5 μm repeatability
- claimed temp stability .1 C
- positioned at (50,100) μm
- Ours: modified to allow in-needle mixing

Precursors

- Metallo-organic
  - Metallocenes (MCp_x, Cp = C_5H_5 ring ligand): $NiCp_2$, $FeCp_2$, $(CH_3)_2PtCpCH_3$
  - Tetrakis (PF_3, triphenylphosphine) metals $Pt(PF_3)_4$, Au, ...
  - Carbonyls $Fe(CO)_5$, $W(CO)_6$, $Mo(CO)_6$, $Ni(CO)_4$, $Co(CO)_3$
  - Fluorides WF_6
  - Chlorides $MoCl_6$
  - Other $[RhCl(PF_3)_2]_2$, $AuClPF_3$ (no P inclusion, self decomposing, 20 $\mu\Omega$cm!),
- Insulators:
  - TEOS (tetraethylorthosilicate) + H_2O

Some applications



- Mask repair / semiconductor circuit editing (in conjunction with IBID)
- Nanosoldering (nanotubes etc.)
- Supertips for AFM and STM, 4 point probes etc.
- Nanowires (contacting, nanocircuits)
- 3D nano construction material
  - Example: tweezers

State of the art

Problematic!

- Serious issues with reproducability
- Nanocomposite metal clusters / precursor fragments
- Non-ohmic, gap can be fitted to IV
- VRH / Mott behaviour found in low temp experiments (are wires photosensitive?)
- But: some good results reported (pure, metallic), *sometimes only below 20K ! ...*
- (trivial) Rate equation established, parameters are the problem (mechanism, dissociation crosssections, reactions, sticking probabilities, diffusion coefficient)
- Monte Carlo calculations (book Joy et al) cut off above the (extremely important) LE SE. STM dissociation @ 20eV!

Project (recipe for success :)

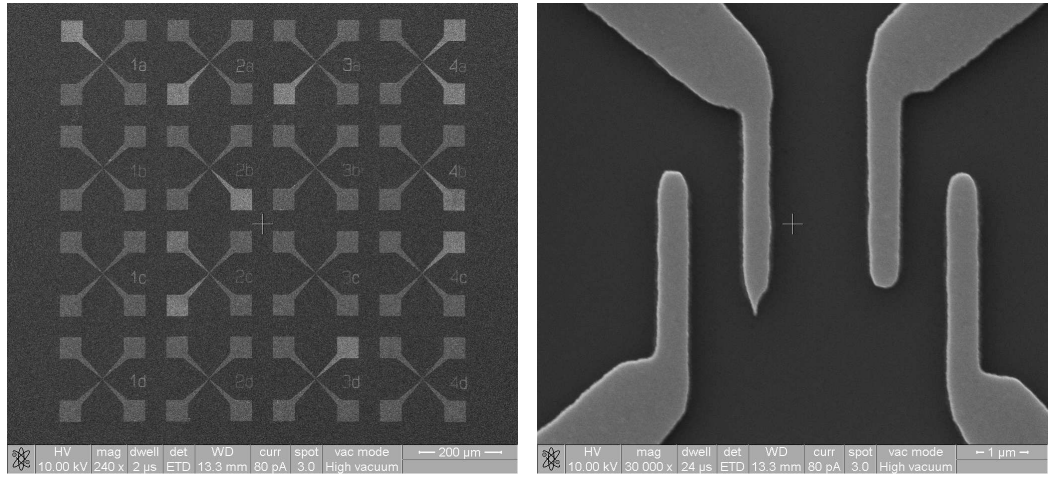
- Improve purity / conductance of EBID nanowires by
  - Robust optimization of beam current, beam voltage, temperature, dwell time, flux
  - Attempt to ban irreproducabilities
  - Explore gas mixing and annealing
- 3 precursors:
  - Std Pt (trimethyl-methylcyclopentadienyl-platinum)
  - Tetrakis Pt $Pt(PF_3)_4$
  - Tetrakis gold or $AuClPF_3$
- Mix in: O_2, H_2O
- Anneal (orders of magnitude improvement in ρ)

Setups

- Gas mixing setup
- Nanopattern samples with e-beam / etchers
- Configure probe station
- EBID / dimension measurements: NanoSEM
- EDX with ZAF / thin film corrections (FEI Acht, NatLab Eindhoven)
- Oven, annealing (NatLab)
- Low temp IV when something good produced (Chip carriers in cryostat would be nice)

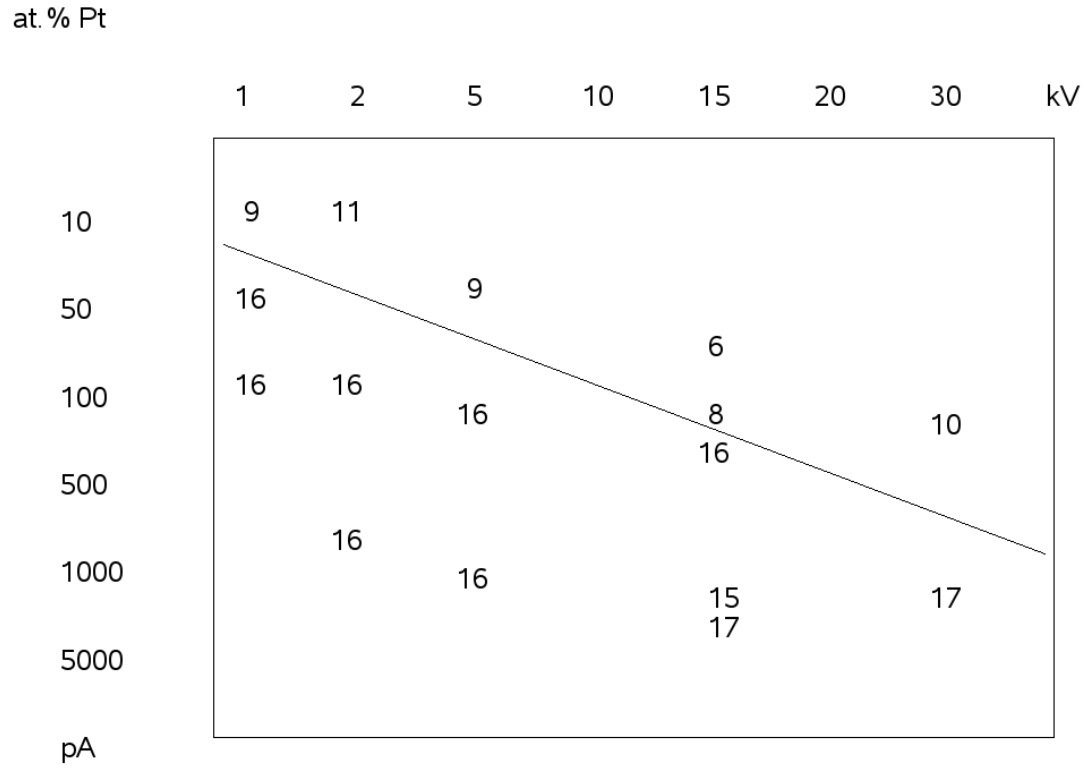
unused ideas: quartz microbalance, tuning fork, in-situ measurements, ...

4 point sample



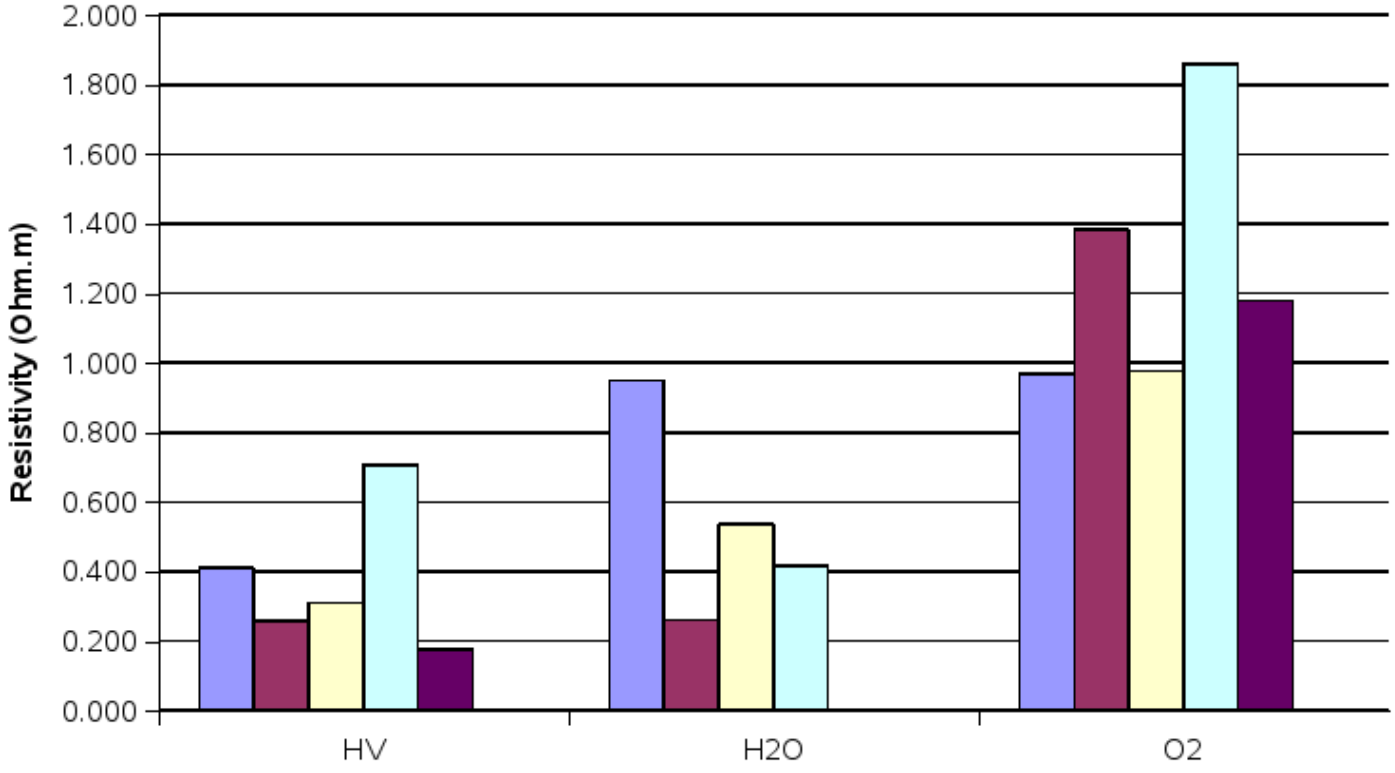
- 2x2 blocks of 4x4 samples per substrate
- Sputter MoGe / 100 nm Au in Z-400
- Write pattern in Ma-N 2405 resist
- Develop in 532/533 mixture, descum (PlasmaLab)
- Etch, IBE, Ar+, strip (PlasmaLab)
- Yield > 90 %

Results: Pt content vs beam



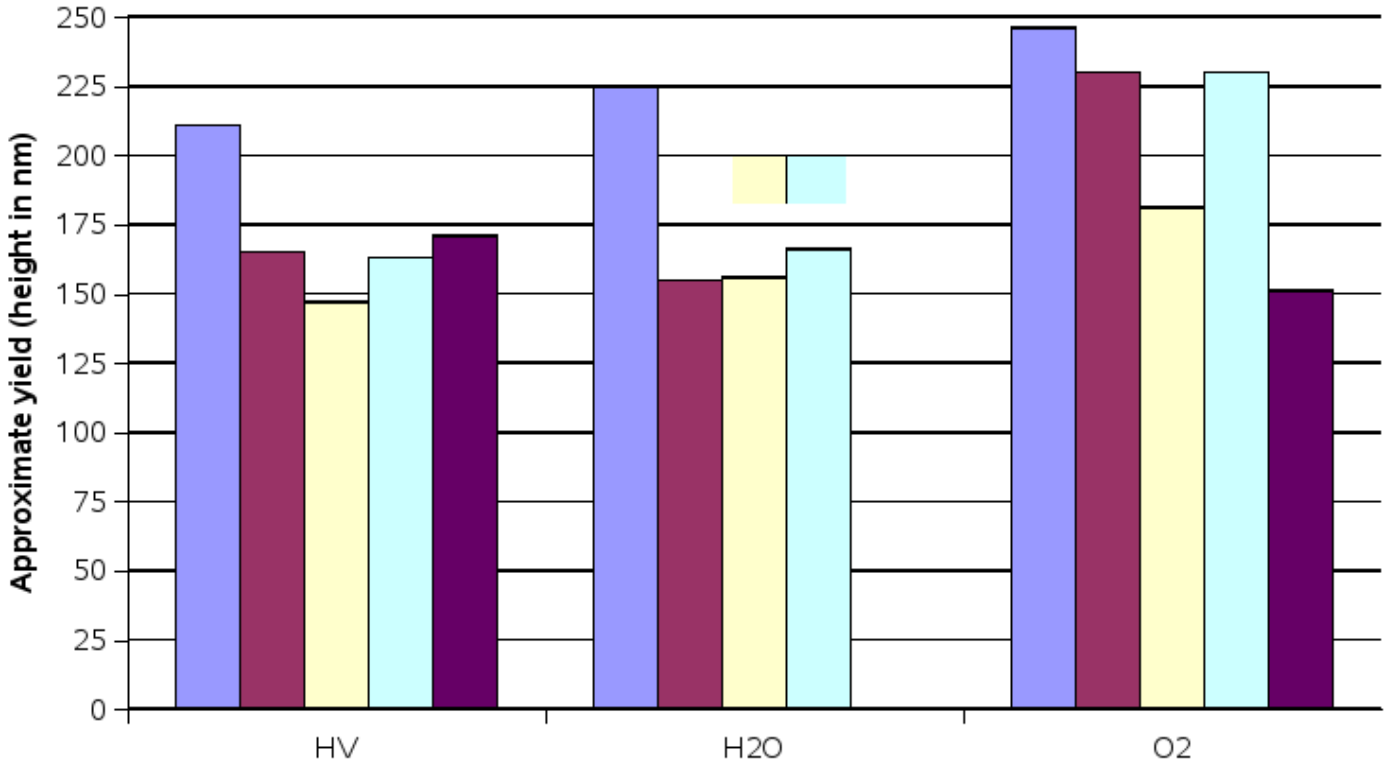
- Bulk analysis, selfconsistent ZAF iteration applied to k-ratios

Results: gas mixing, ρ



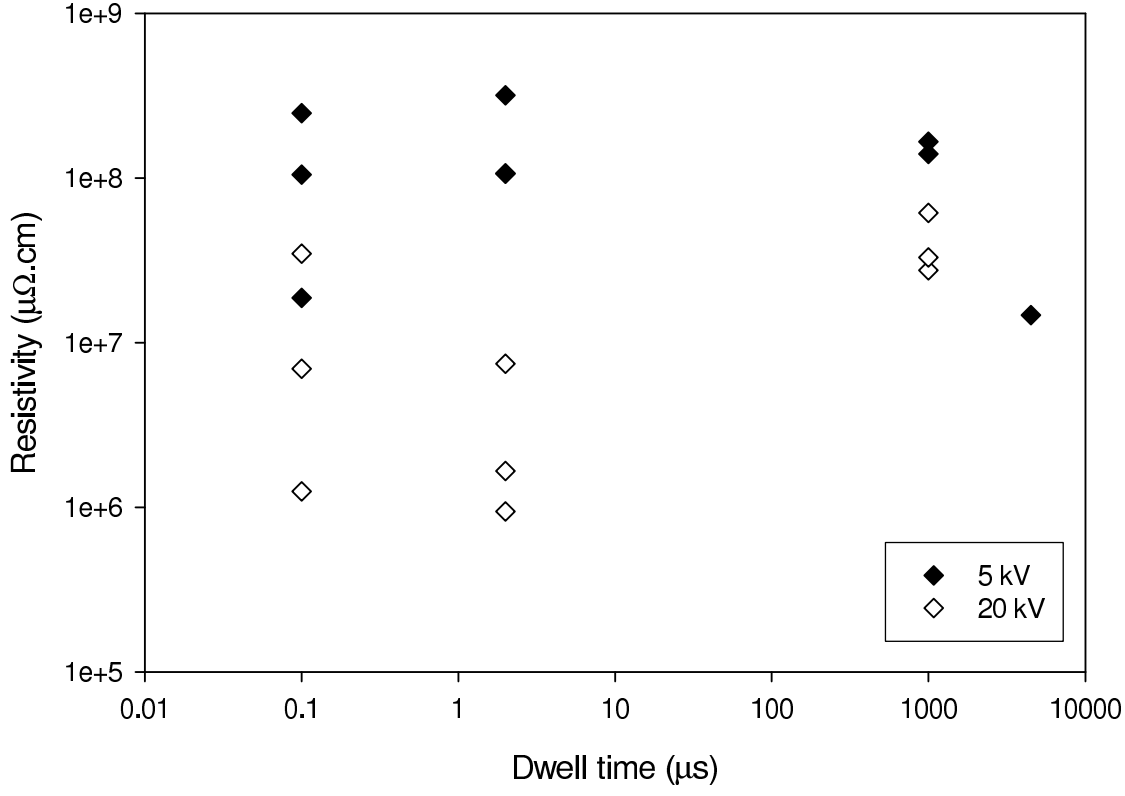
- Std Pt, deposition @ 5kV, UHR mode, beam nominal 900 pA, actual 570 pA, 2 min, 8500x800 nm, 1μs dwell, 0% overlap, , 0% rel diam
- Lots of scatter. Only small variations in Pt conc!

Results: gas mixing, yield



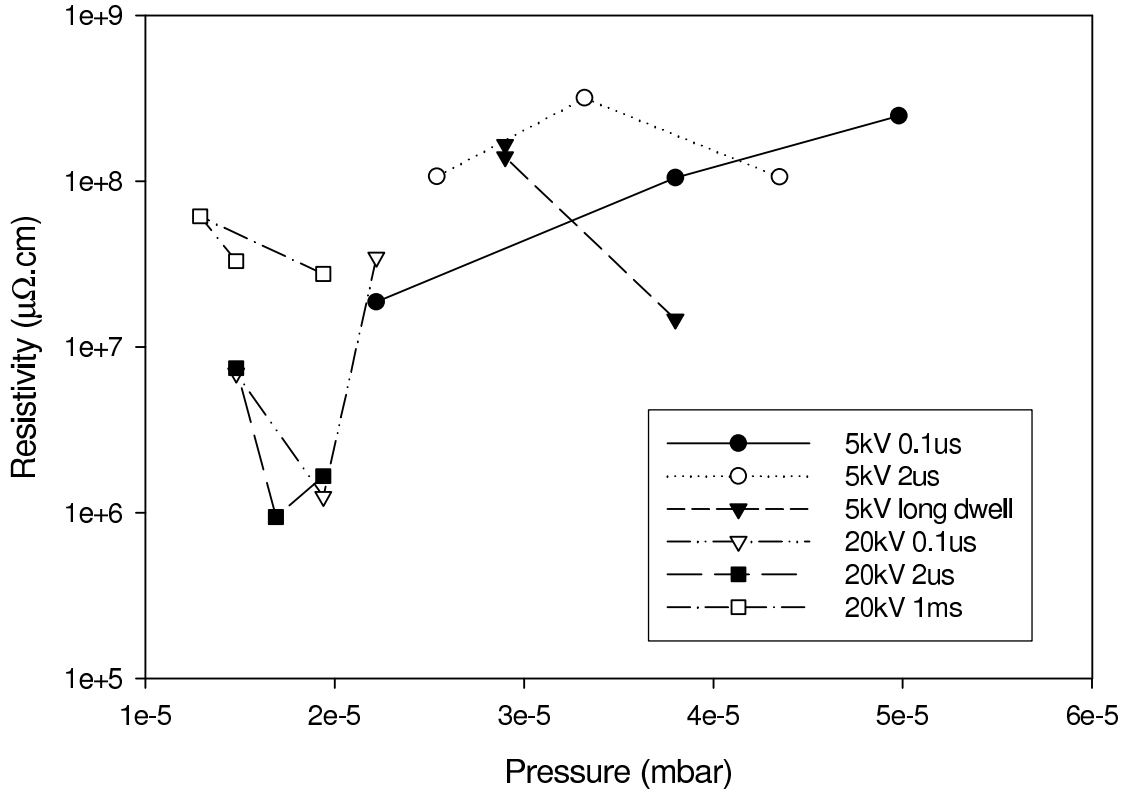
- Std Pt, deposition @ 5kV, UHR mode, beam nominal 900 pA, actual 570 pA, 2 min, 8500x800 nm, 1μs dwell, 0% overlap, , 0% rel diam
- $\sigma(Yield) < \sigma(\rho)$

Results: dwell time experiment



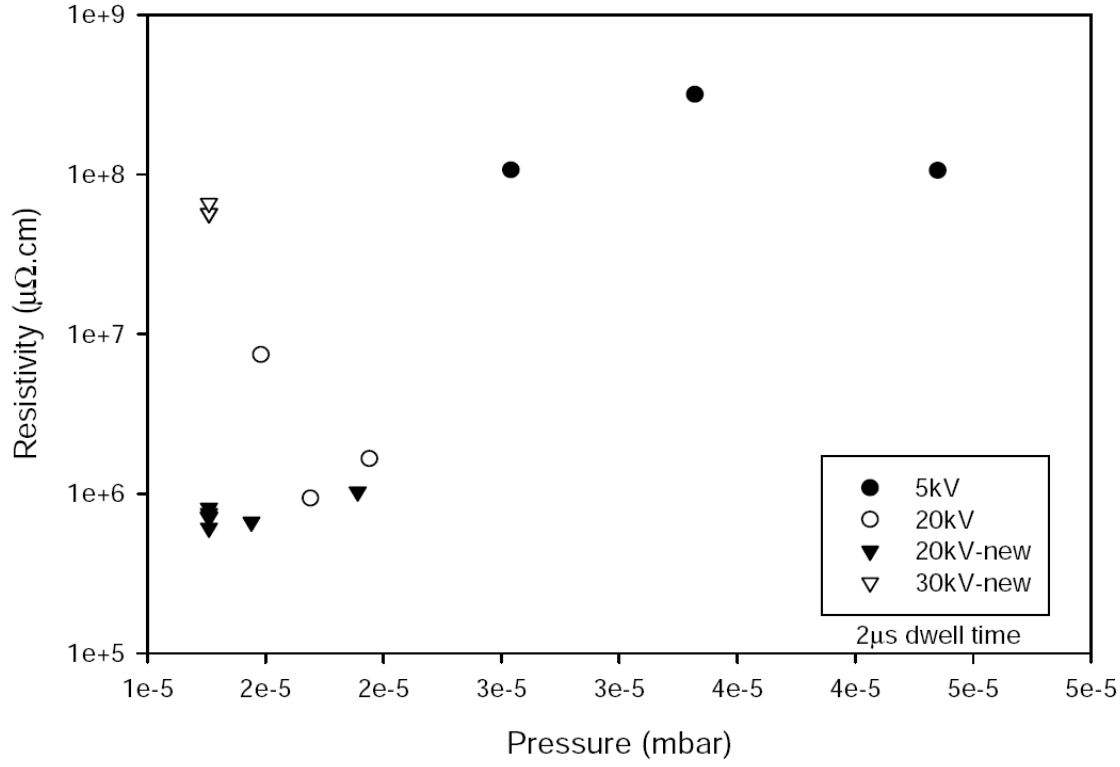
- Std Pt, deposition @ spot 5, (5,20) kV, 8500x800 nm, 0% overlap, , 0% rel diam
- Results span 4 orders of magnitude

Results: dwell time experiment



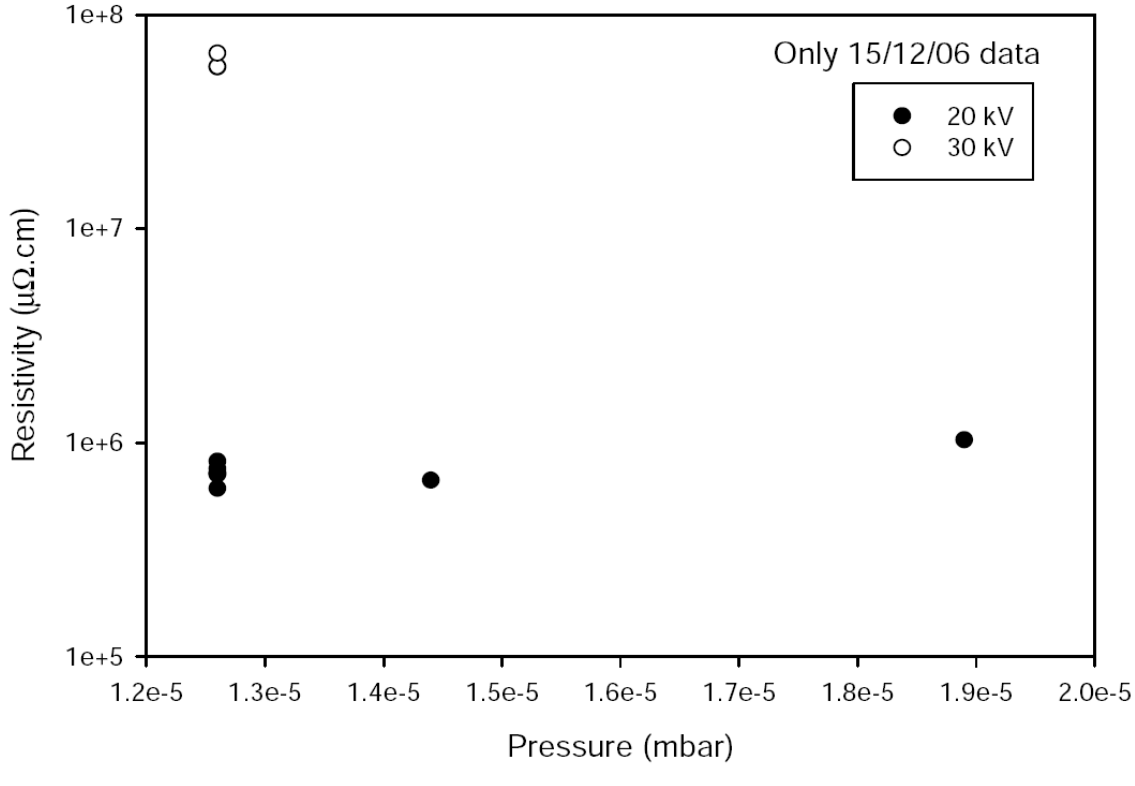
- Std Pt, deposition @ spot 5, (5,20) kV, 8500x800 nm, 0% overlap, , 0% rel diam
- Clear correlation with (unstable) pressure/flux!

Results: Try to stabilize pressure



- New data: keep GIS open, GIS seems to have an issue with flow stability

Results: 5 kV low pressure data



- almost 4 orders of magnitude improvement by choosing beam kV, current, dwelltime, pressure
- reproducible process

Conclusions

- GIS flow unstable. Flow determined by volume at pressure p which is determined by T (Clausius Clapeyron: $ln(p) \sim 1/T$) and conductance
- It seems we are just entering the flux limited regime... Crossover flux-limited / current-limited must be determined
- Improve GIS. MFC?
- Chamber must be in defined state (ozone cleaner will be mounted)
- Several orders of magnitude improvement so far, *10 kΩ resistances can soon be expected without gas mixing or annealing*
- We are now in a good position to investigate gas mixing and annealing