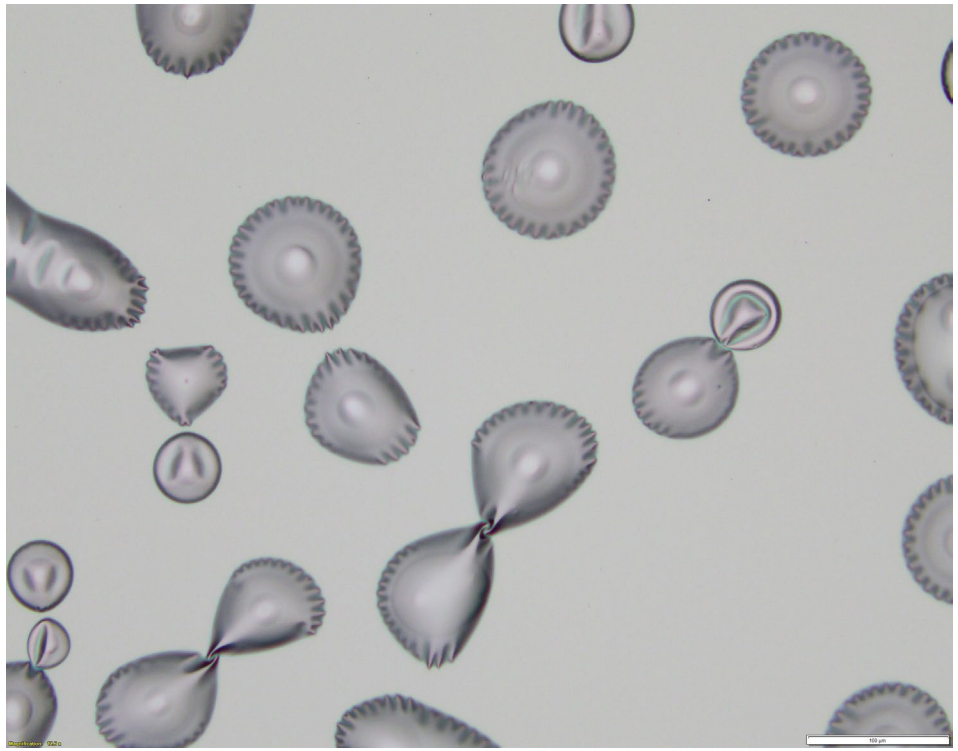
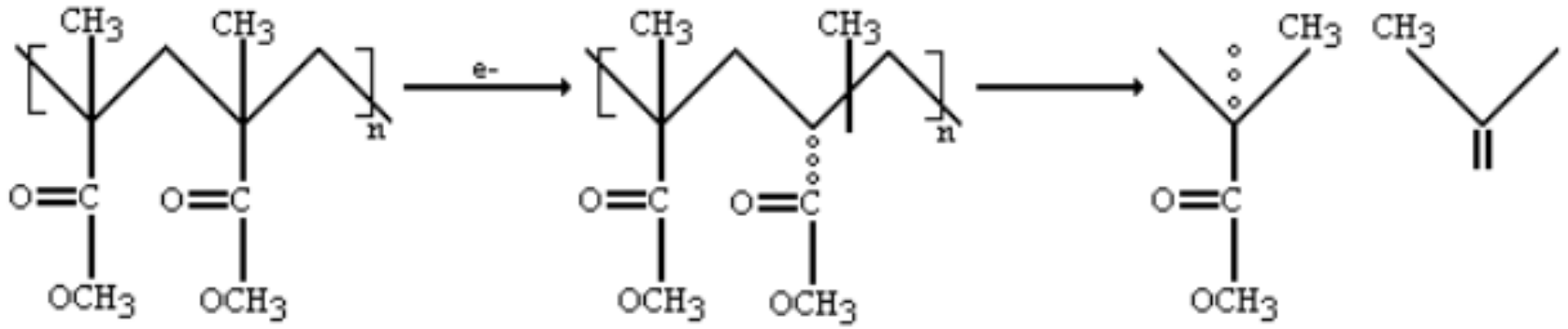
Understanding and Mitigating PMMA Bubbling



David Barth
UPenn
QNF, Singh Center
2023/09/14

PMMA e-beam resist

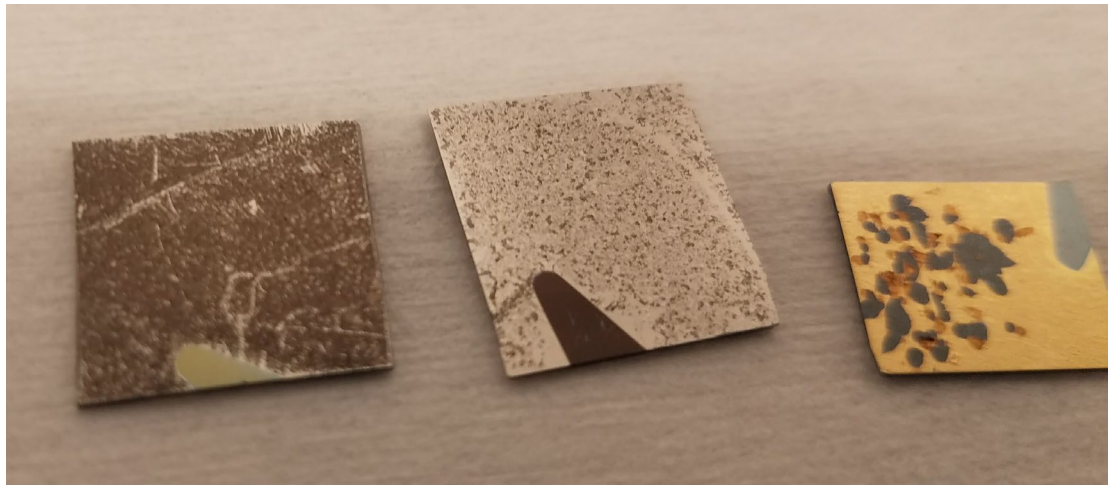
- Cheap, high resolution e-beam resist
- Good for liftoff, bad for etching
- Exposure causes chain scission
  - Lowers molecular weight
  - Polymer becomes more soluble

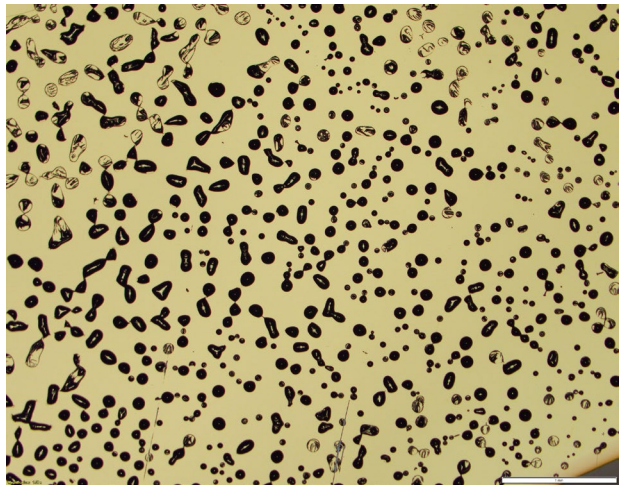


S. Lewis and L. Piccirillo, 'Influence of Nanocomposite Materials for Next Generation Nano Lithography', Advances in Diverse Industrial Applications of Nanocomposites. InTech, Mar. 22, 2011. doi: 10.5772/15624.

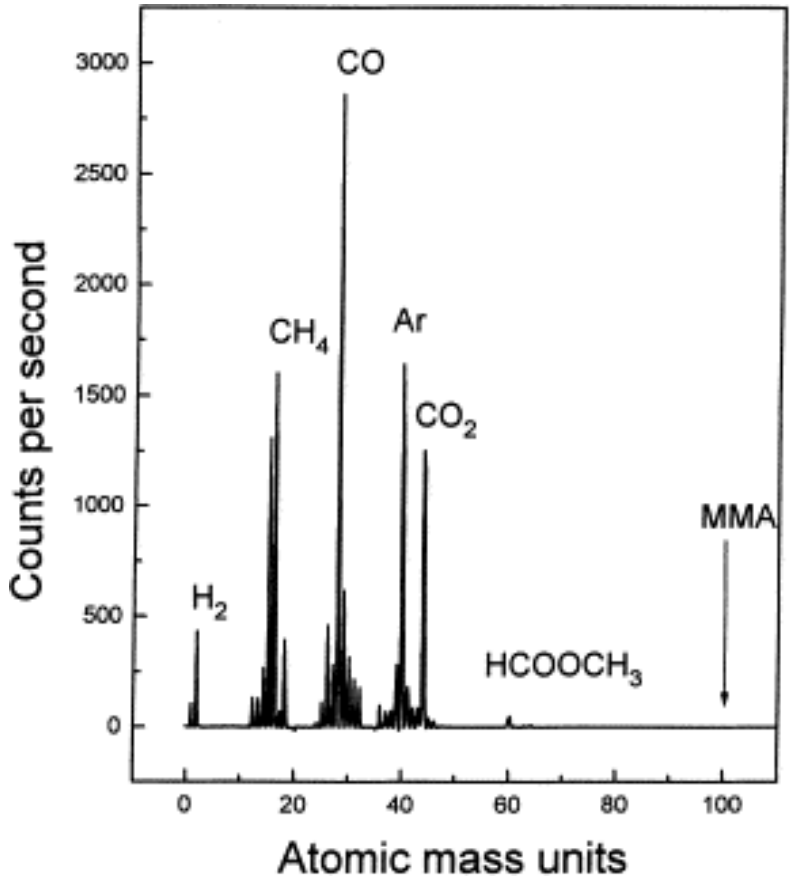
PMMA Bubbling

- Bubbling happens when volatile byproducts of chain scission are trapped between PMMA and a thin film
- Usually during e-beam evaporation
- Can also be an issue during EBL (especially alignment) if sample is coated for charge dissipation



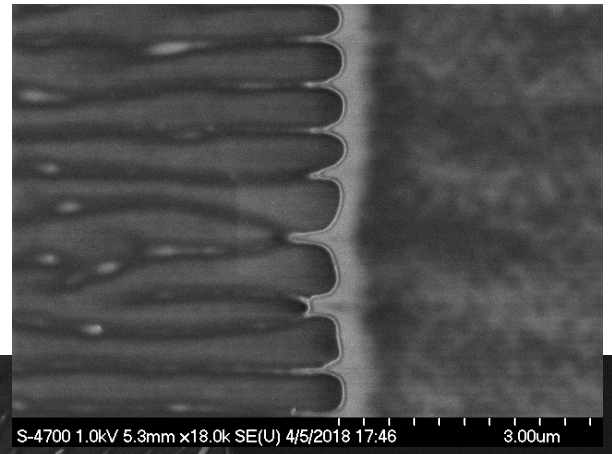


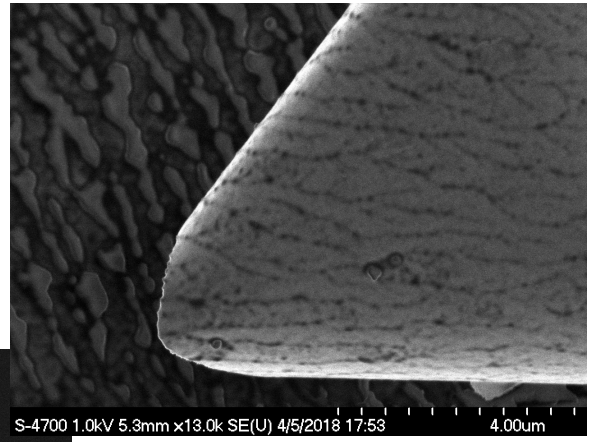
PMMA Chain Scission Byproducts



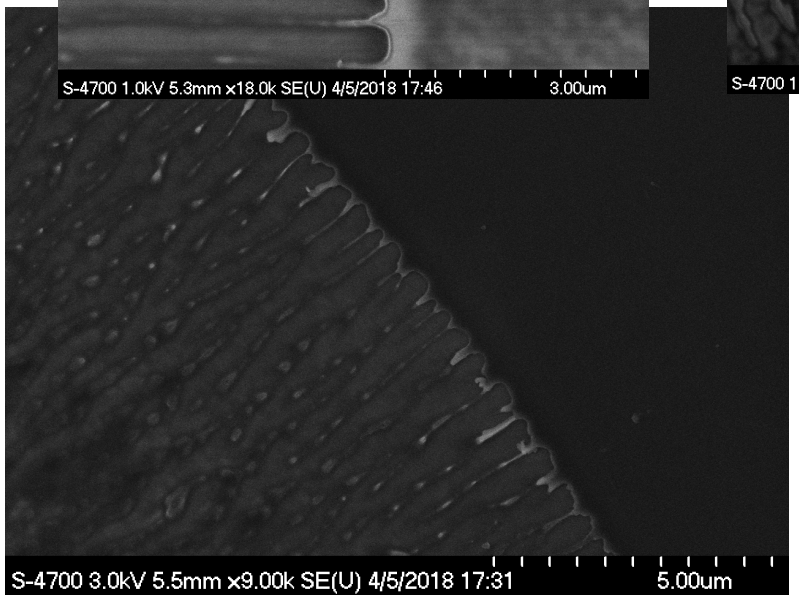
M.E Fragalà, G Compagnini, L Torrisi, O Puglisi, Ion beam assisted unzipping of PMMA, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 1998, https://doi.org/10.1016/S0168-583X(98)00087-1.

What does it look like?

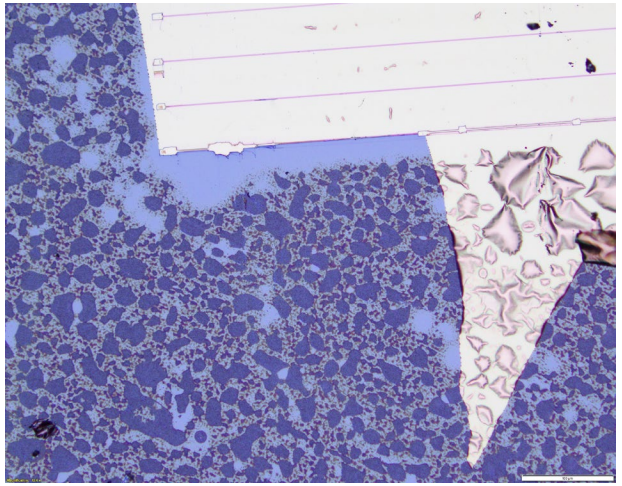


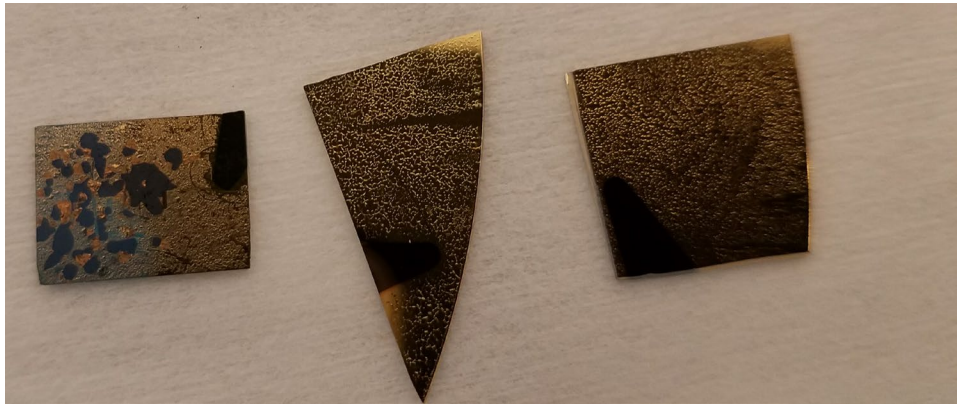


Ti/Pt



Ti/Au



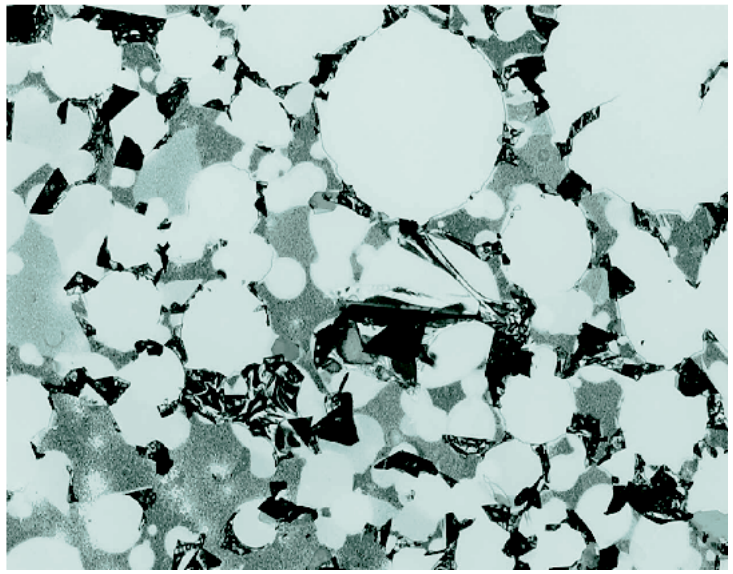


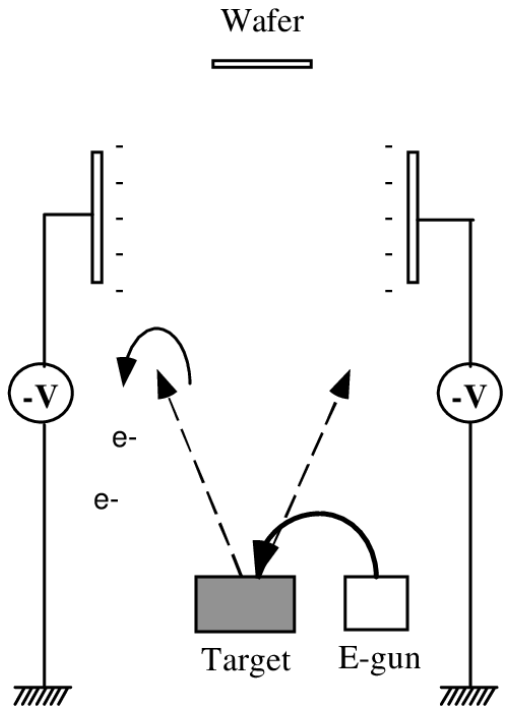
Ti/Au

What doesn’t cause bubbling?

- Heat
- Bremsstrahlung x-rays
- Expired/contaminated resist
- Developers
- EBL hardware problems
- Magic
- **Anything except charged particle irradiation!**

Some Experiments





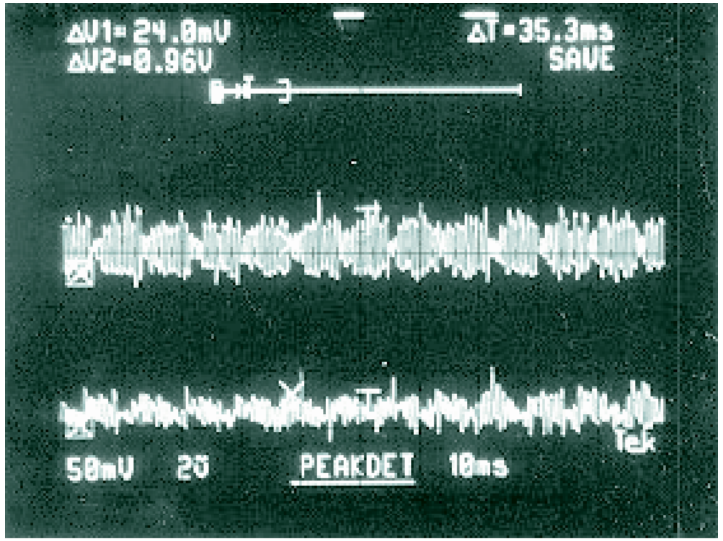
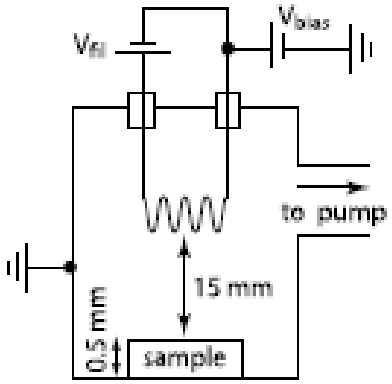


Figure 2. Free electron signal (i.e., current) generated inside the chamber during platinum evaporation

Pao, Y. C. et al. “Solution to the E-beam Gate Resist Blistering Problem of 0.15 micron PHEMTs.” CSMANTECH (1999).

Some Experiments



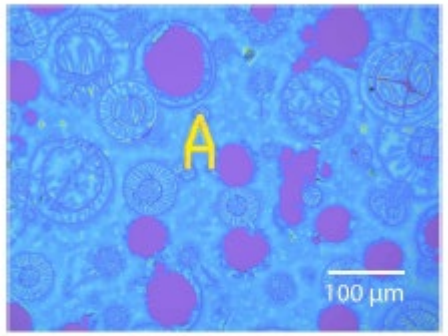


Figure 7. Optical image of a Si^{++}/SiO_2 substrate with a gold marker and spin coated PMMA layer, which was exposed two times to the electron bombardment described in figure 6 at a bias voltages of $V_{bias} = 0$ V. Both the size and the shape of the bubbles and blisters are comparable to the sample with the resist problems in figure 5(a), which was metalized in an e-beam evaporator.

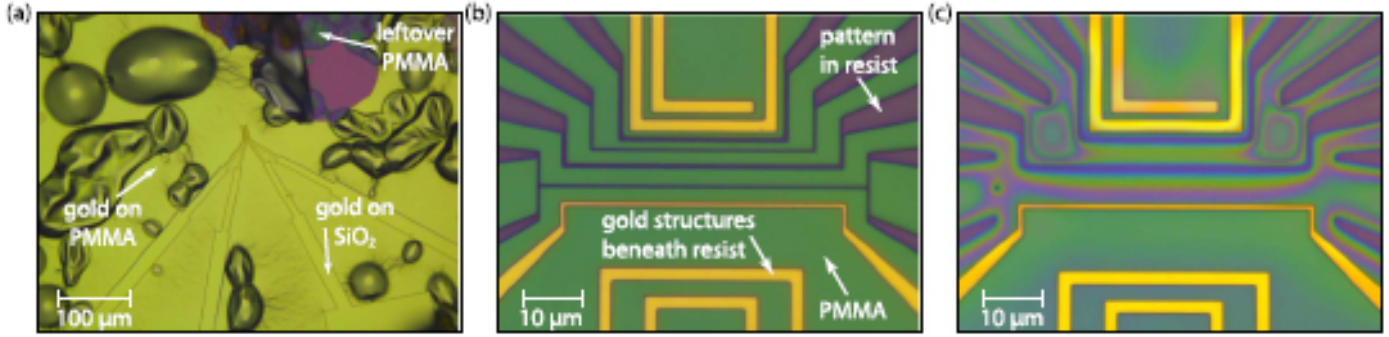


Figure 5. (a) Optical microscope image of a structure defined in a PMMA resist layer by electron beam lithography directly after the metallization process in an e-beam evaporator which had the problem of a high secondary electron emission. In places where the bubbles and blisters in the metal layer burst open, it is observed that the PMMA underneath these bubbles is partially gone. (b) A patterned structure written in a double layer resist layer spin coated on a Si^{++}/SiO_2 substrate already having gold structures. (c) Same sample as in (b) after heating the sample above the glass transition temperature of PMMA (around 105 °C) which destroyed the smallest pattern in the resist.

Frank Volmer, et al.; How to solve problems in micro- and nanofabrication caused by the emission of electrons and charged metal atoms during e-beam evaporation. *J. Phys. D: Appl. Phys. 54* March 2021.

Some Experiments

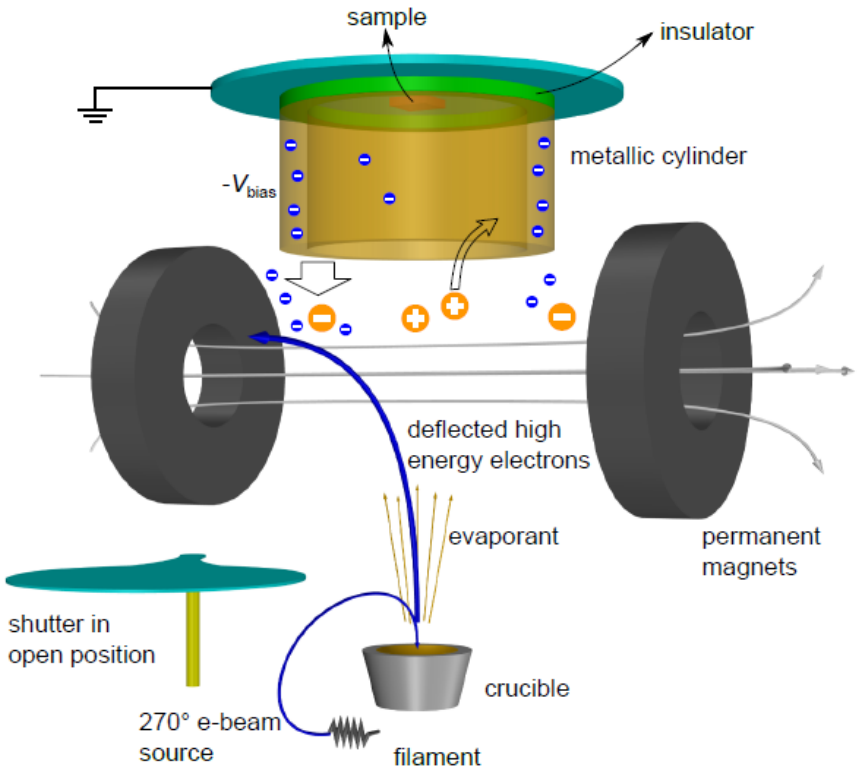
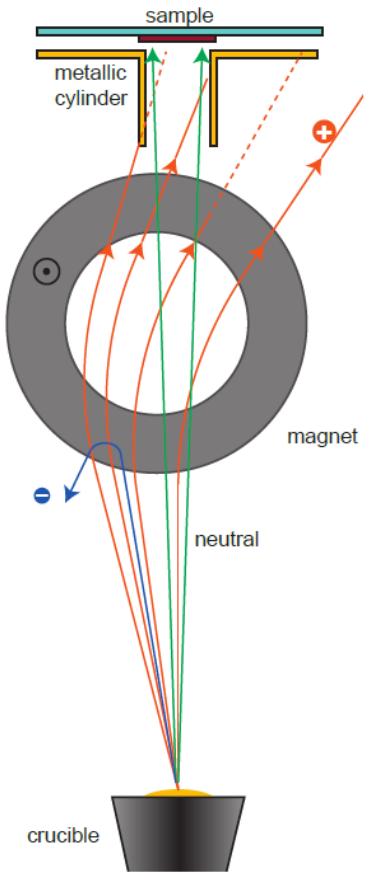
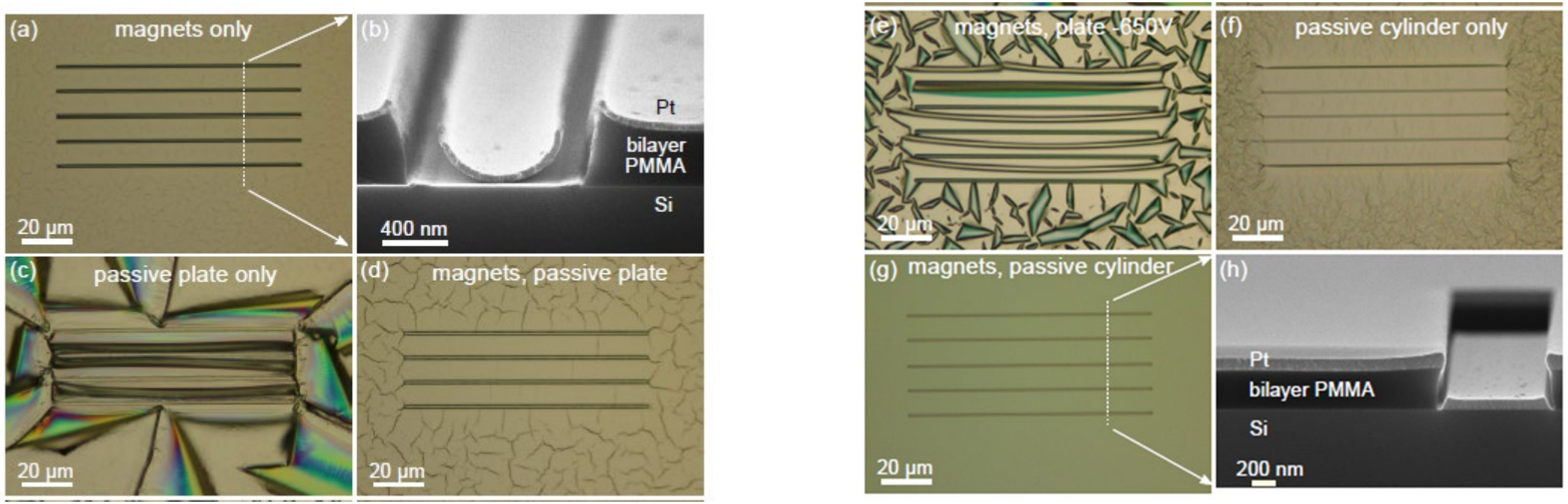


FIG. 3. Schematic (dimension is not to scale) of the improved electron beam evaporation setup with permanent magnets and an insulated metallic cylinder installed to avoid electron radiation on sample surface.



Bin Sun, et al.; Role of electron and ion irradiation in a reliable lift-off process with electron beam evaporation and a bilayer PMMA resist system. *J. Vac. Sci. Technol. B* 1 September 2021; 39 (5): 052601.

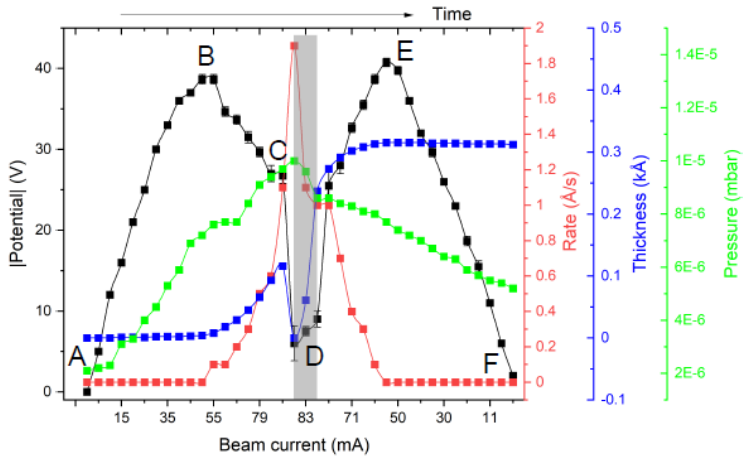
Some Experiments



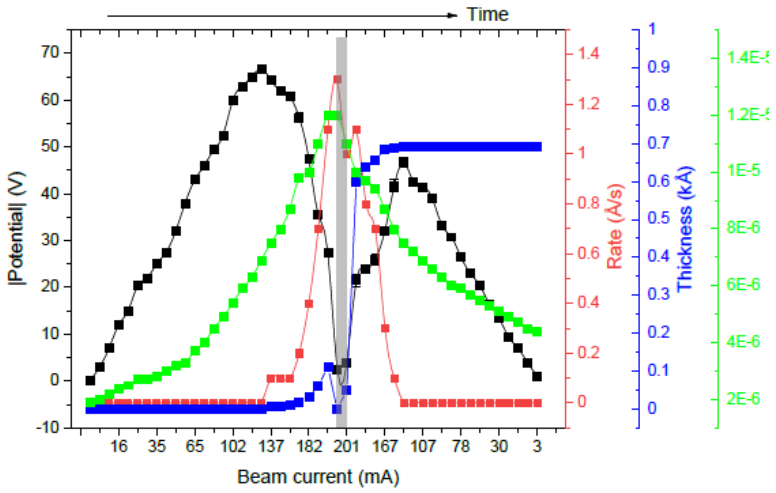
Bin Sun, et al.; Role of electron and ion irradiation in a reliable lift-off process with electron beam evaporation and a bilayer PMMA resist system. *J. Vac. Sci. Technol. B* 1 September 2021; 39 (5): 052601.

Some Experiments

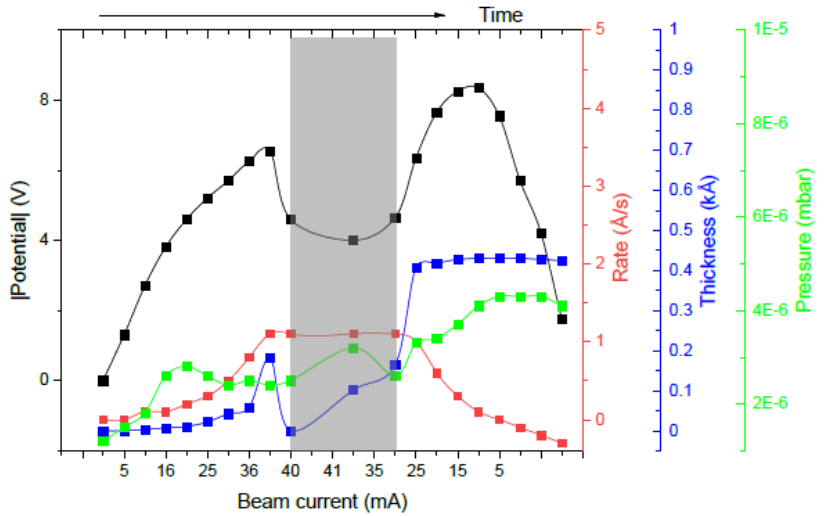
Potential at floating cylindrical electrode (note y axes)



Pt



Au



TiO_2

Bin Sun, et al.; Role of electron and ion irradiation in a reliable lift-off process with electron beam evaporation and a bilayer PMMA resist system. *J. Vac. Sci. Technol. B* 1 September 2021; 39 (5): 052601.

Conclusions

- Low energy electrons are largely responsible
- Ionized deposition material may also contribute
- Heat and x-rays negligible
- Charged particle irradiation is highly dependent on chamber geometry, shutter arrangement, source, recipe

How to fix it?

- Build a very complicated setup within your chamber to reject charged particles
  - At Penn, most of these would probably violate safety rules
- Get a new evaporator with a design less prone to irradiating samples
- Try to mitigate issue with smaller measures:
  - Magnets
  - Shielding
  - Source management
  - Recipe modifications
  - Increase throw distance (maybe)

Source Management

- Crucible material matters
  - Carbon contamination greatly increases electron scattering
  - No carbon/Fabmate for Au, Pt
  - Metal surface can be cleaned
- Spacers under crucible to reduce power required

- Thermodynamic style crucible

Recipes

- Reduce total beam-on time (even with closed shutter)
  - Increase deposition rate
  - Speed up ramps
  - Shorten soaks
- Fixed spot instead of sweep
  - Usually gives higher rate at lower power
- Optimize PID to reduce shutter delay

Case Study #1

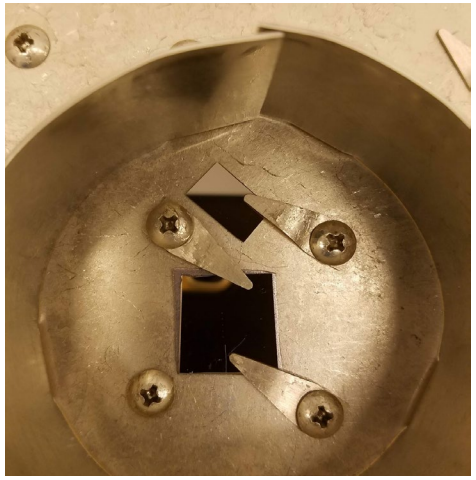
Angstrom NexDep (~2016)

- Open-load system
- 6 pocket hearth
- 7 cc liners
- ~20 cm throw
- Single shutter at sample
- Water cooled platen
- Bubbling issue was severe for Au, Pt, Pd

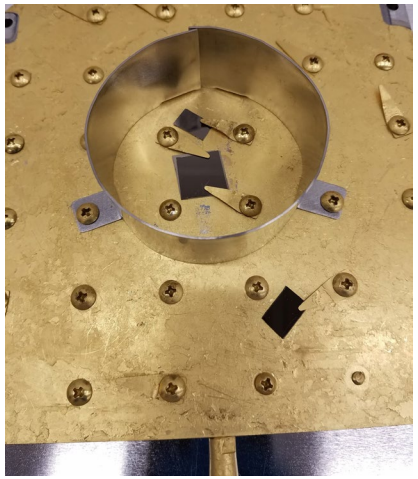
Case Study #1- Resolution

- Vendor was convinced it was thermal issue
- Z stage installed to allow longer throw
  - This actually made it worse
- I demonstrated that PMMA was fully exposed even with shutter closed for entire recipe
- Fabricated cylindrical shield to protect sample when shutter was closed
  - This solved problem except in extreme cases

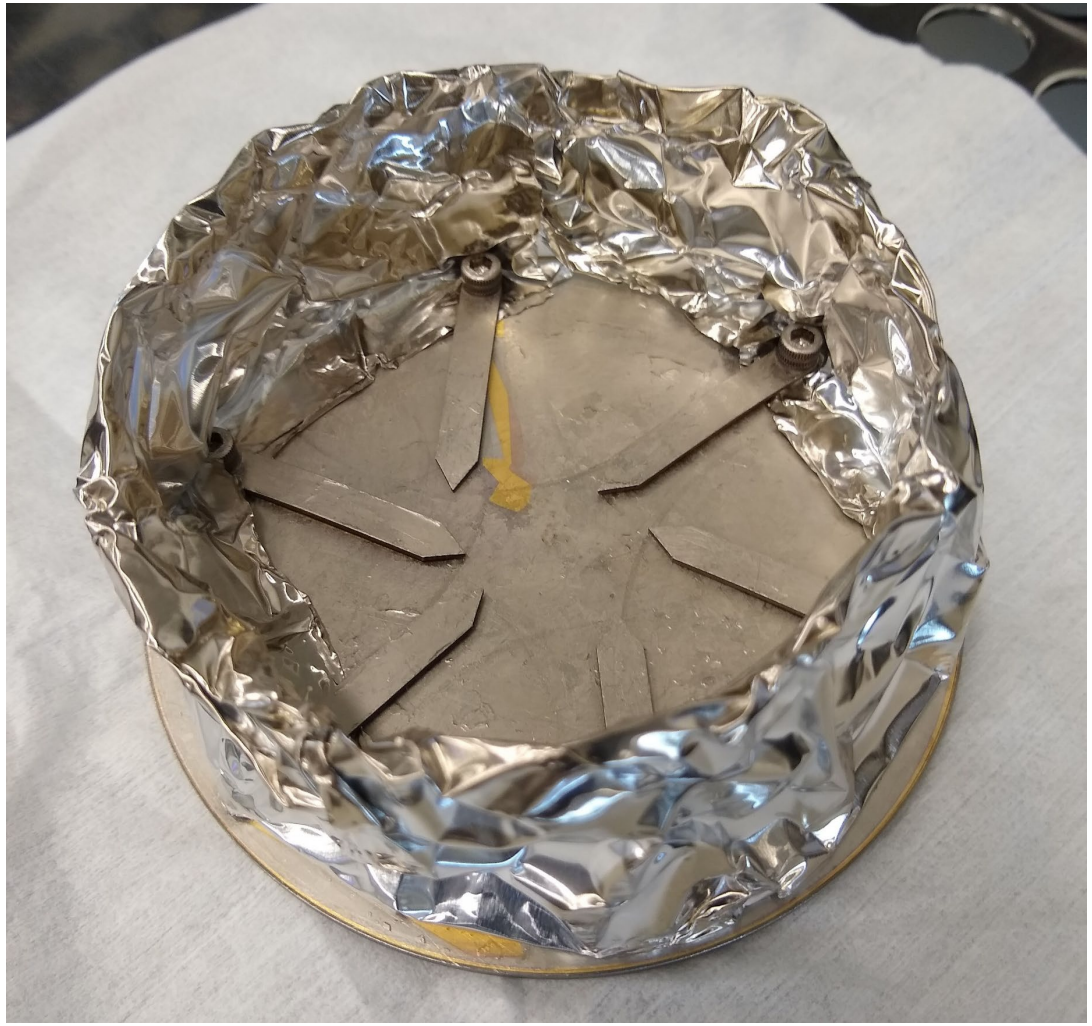
Outside shield



Inside shield



This solution works on other systems



Case Study #2

Custom Angstrom System

- Dual chamber design
- 6 pocket hearth, 15cc
- ~30 cm throw
- Single shutter at source + gate valve
- Resolution:
  - Confirmed that damage occurred before shutter open
  - Modified recipe to leave gate valve closed until immediately before shutter opened
    - Fully resolved problem

Final Thoughts

- Bubbling is caused by irradiation of sample by charged particles
- Mitigating bubbling involves:
  - Reducing charged particle generation
  - Shielding sample from charged particles
- This can be done in many ways
- What works best is probably highly tool dependent

Penn
University of Pennsylvania

Thoughts?