SAND2024-06143C

Sandia National Laboratories

Exceptional service in the national interest

Combinatorial synthesis and high-throughput characterization of Cu-Ag and Ni-Pt thin films fabricated by confocal magnetron sputter deposition

K.R. Dorman, N. Bianco, R. Kothari, M. Kalaswad, C. Sobczak, S. Desai, J. Custer, S. Addamane, M. Jain, A. Hinojos, F. DelRio, B. Boyce, R. Dingreville, D.P. Adams

Beyond Fingerprinting

International Conference on Metallurgical Coatings and Thin Films 2024

U.S. DEPARTMENT OF ENERGY NNSA National Nuclear Security Administration

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Goals:

- **Develop the means and methods to apply machine learning to materials development.**
- Automate and speed up growth, measurements, and analysis.
- Inter-relate between process conditions, resulting structure, and desired properties.
- Survey the results for optimal performance and determine how to grow even better films.

Primary Tools:

- Combinatorial deposition and automated mapping equipment.
- SIMTRA for linking process conditions to atomistic simulations.
- Workflow tools for tracking samples and progress and visualization tools for the dataset.
- Machine learning to link desired structure and properties to growth conditions.

Properties

Nanoindentation, AFM, 4 Point Probe, Optical Profilometry

Hardness, Reduced Modulus, Roughness, Resistivity

Process

Growth Conditions, SIMTRA, SRIM

Energy, Angle, Pressure, Working Distance, Racetrack…

Structure

XRR, XRD, WDS

Grain Size/Orientation, Composition, Density

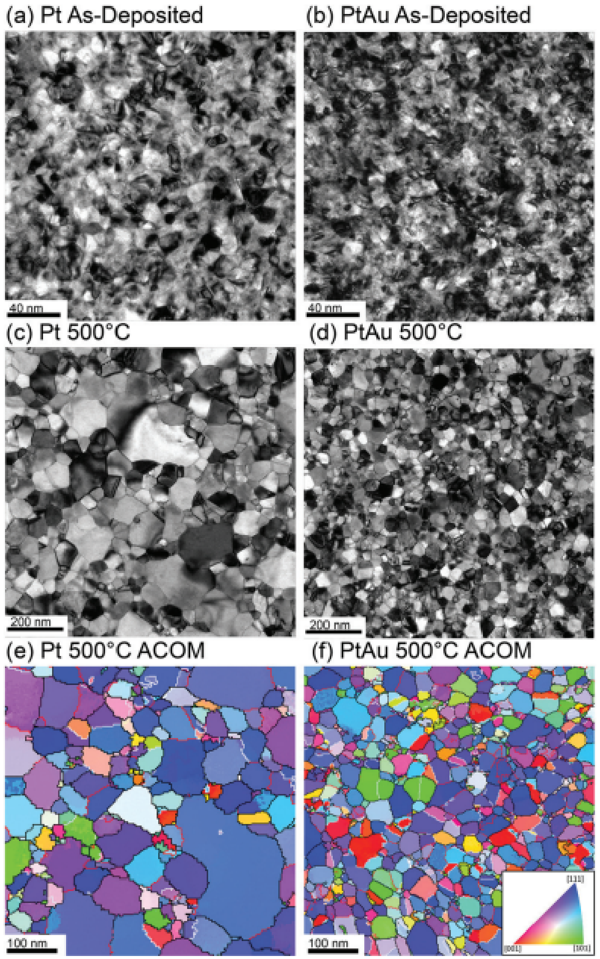
Case Study: Full compositional survey of binary metal nanocrystalline thin films

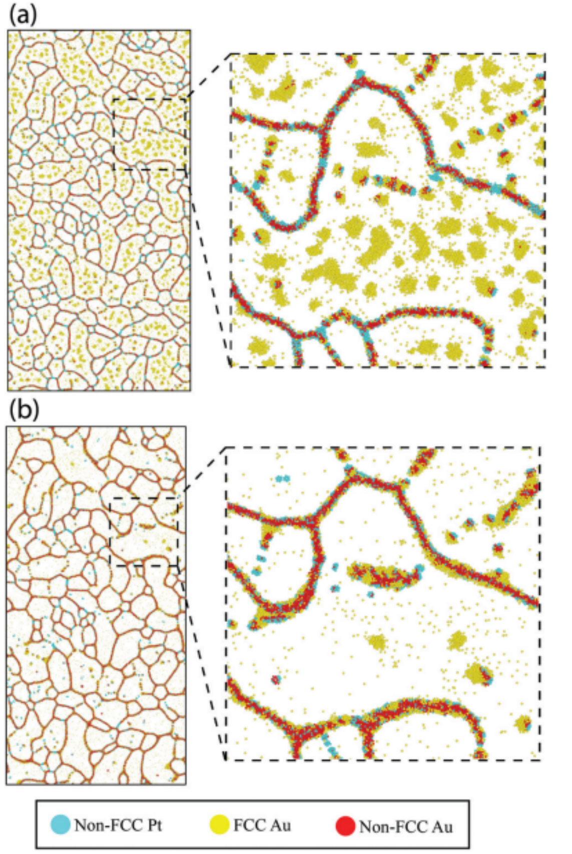
- Why a **high throughput survey** on **nanocrystalline materials**?
  - Enhanced or altered properties coming from grain structure.
  - Comparatively hard to simulate and predict stability.
  - Easy to sputter as nanocrystalline, though (often) unstable.
- Where is the bottleneck to survey speed?
  - Historically, with deposition, vacuum and high film quality requires hours to days.
  - Modern measurement of a macroscopic material property can takes minutes or less.
- What is the fix?
  - Grow many compositions with very few depositions.
- How high-throughput does this get?
  - In this experiment, more than 100 times faster than the traditional approach!

Nanocrystalline Stability

- Nanocrystalline materials may enhance mechanical properties.
    - Hall-Petch strengthening
- Grain growth mechanisms destabilize it.
    - Thermal growth limits viable materials.
    - Mechanical stress-driven growth interferes with the desired applications.
- Grain growth can be mitigated.
    - Zener or void pinning
    - Solute drag
    - Grain-boundary segregation

Why the interest in binary metal systems?



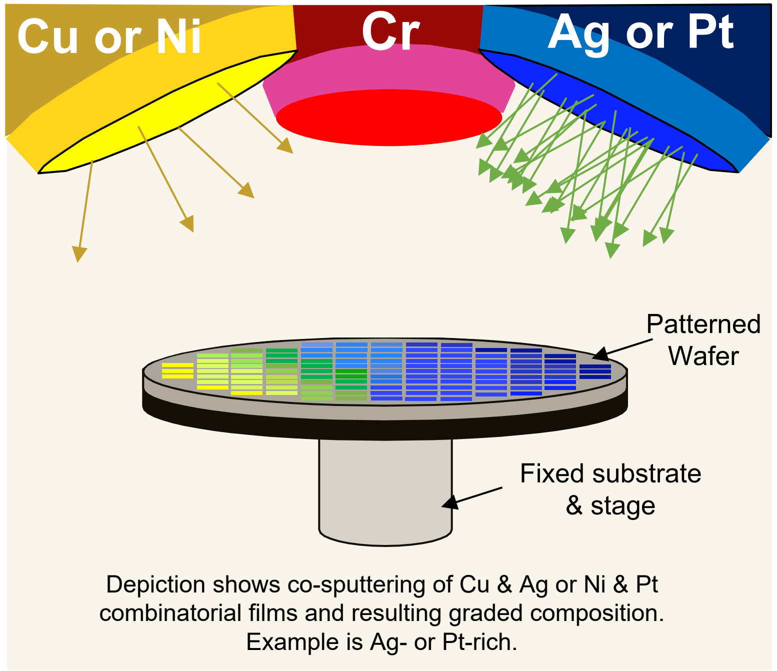


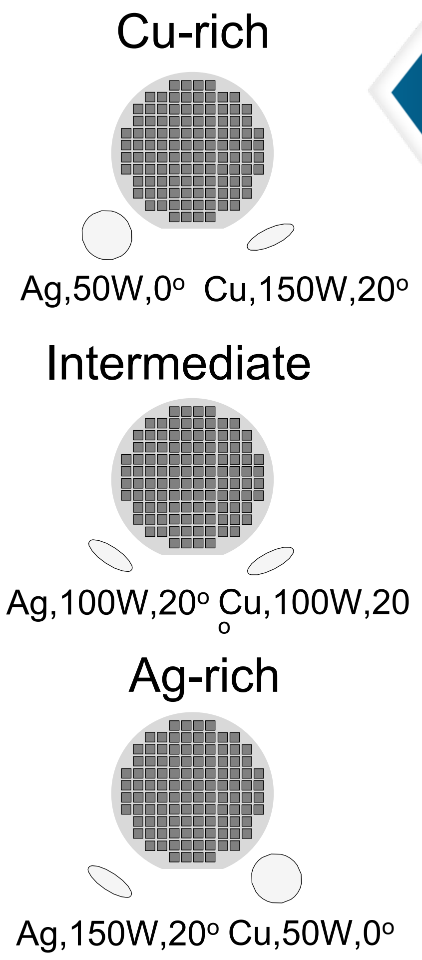
ig. 5 For the Pt–10Au NC atomistic system, snapshots depicting the emporal evolution of Au after (a) 0.25 ns and (b) 20 ns of MC-MD simu- ations at 500 °C. The insets show close-up views of a region where Au phase separates in the bulk Pt grains during the initial stages of thermal annealing then continues to segregate to GBs at late stages. FCC Pt atoms are deleted for a better visualization of the structures.

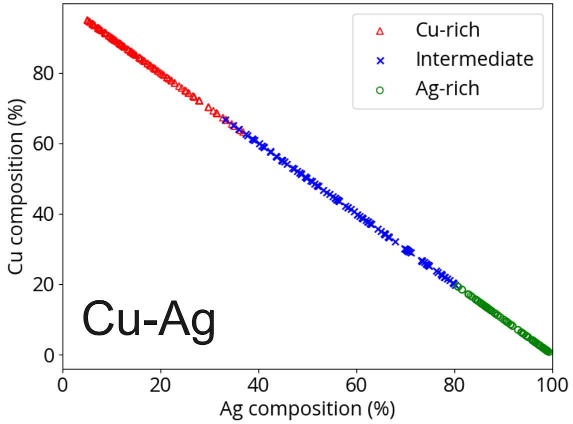
Barr et al. (2021) *Nanoscale*

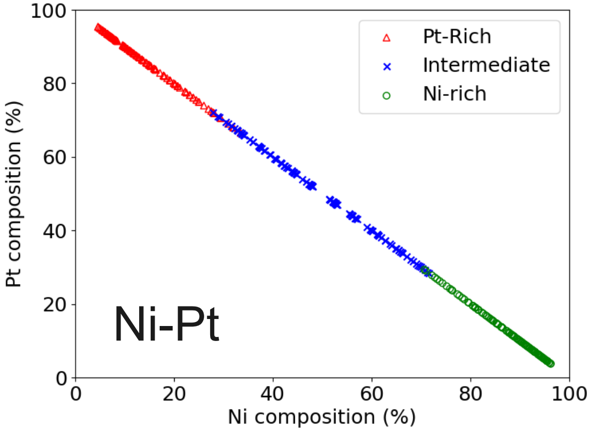
Combinatorial Synthesis

- Fixed stage + confocal system = compositional gradient.
- Photolithography: one graded film becomes many small films.
- Change gun angle to grow extremal compositions.
- A 150 mm / 6” wafer can comfortably fit 112 1 cm^2 samples!

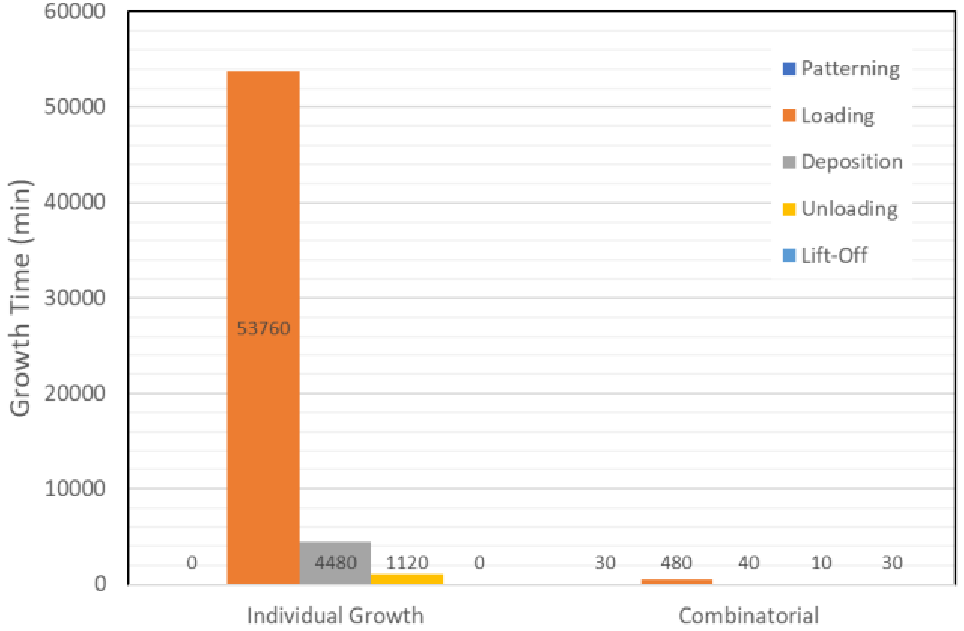


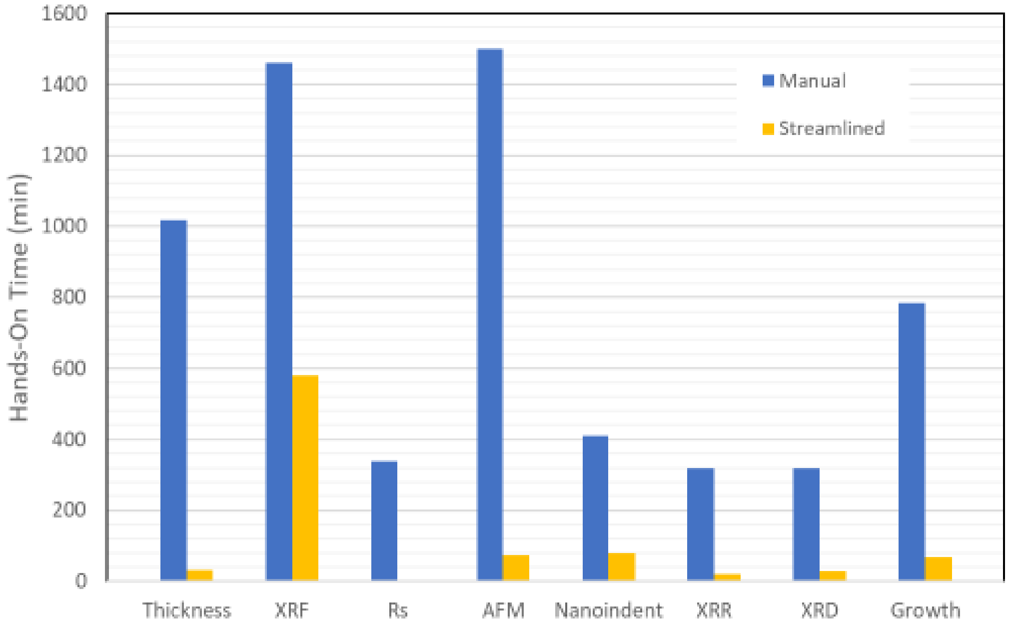


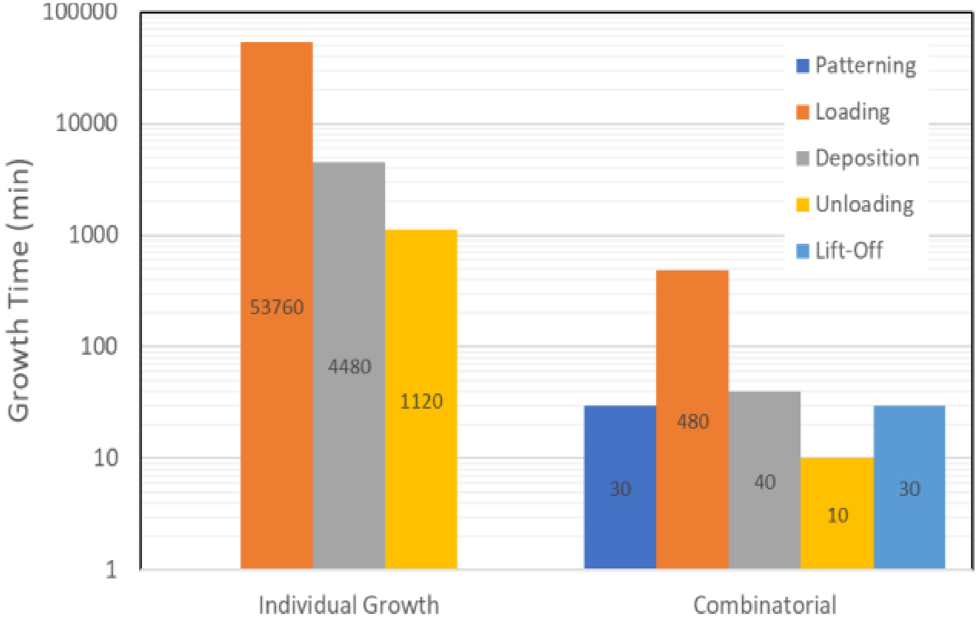


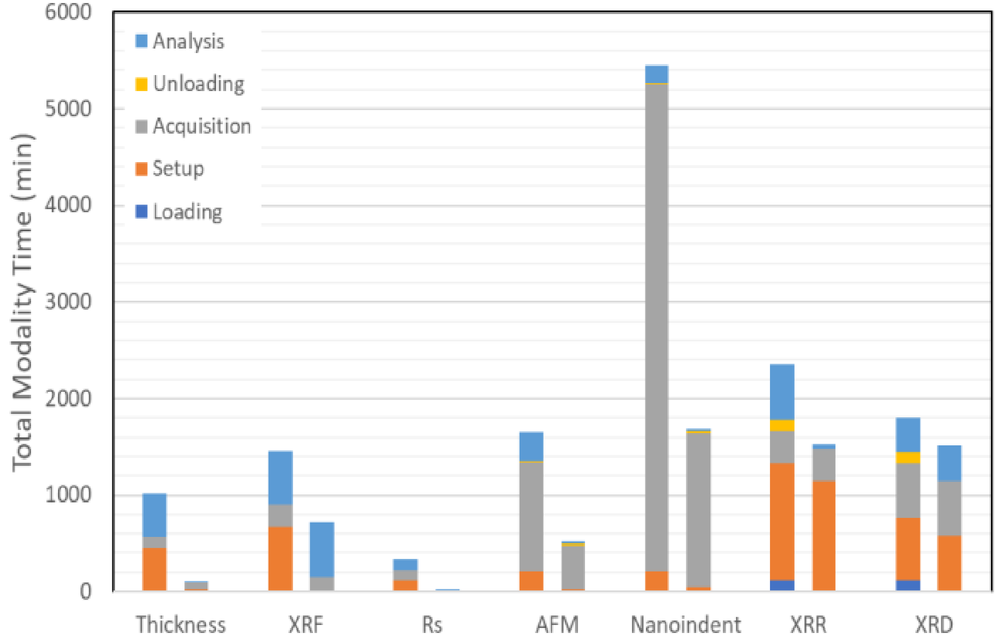


How Fast Can This Actually Go?









- **Deposition is no longer the bottleneck**!
- Times are for growing or measuring 112 samples.
- Much hands-on time is saved by programming and automated measurements.

Planning Depositions Efficiently

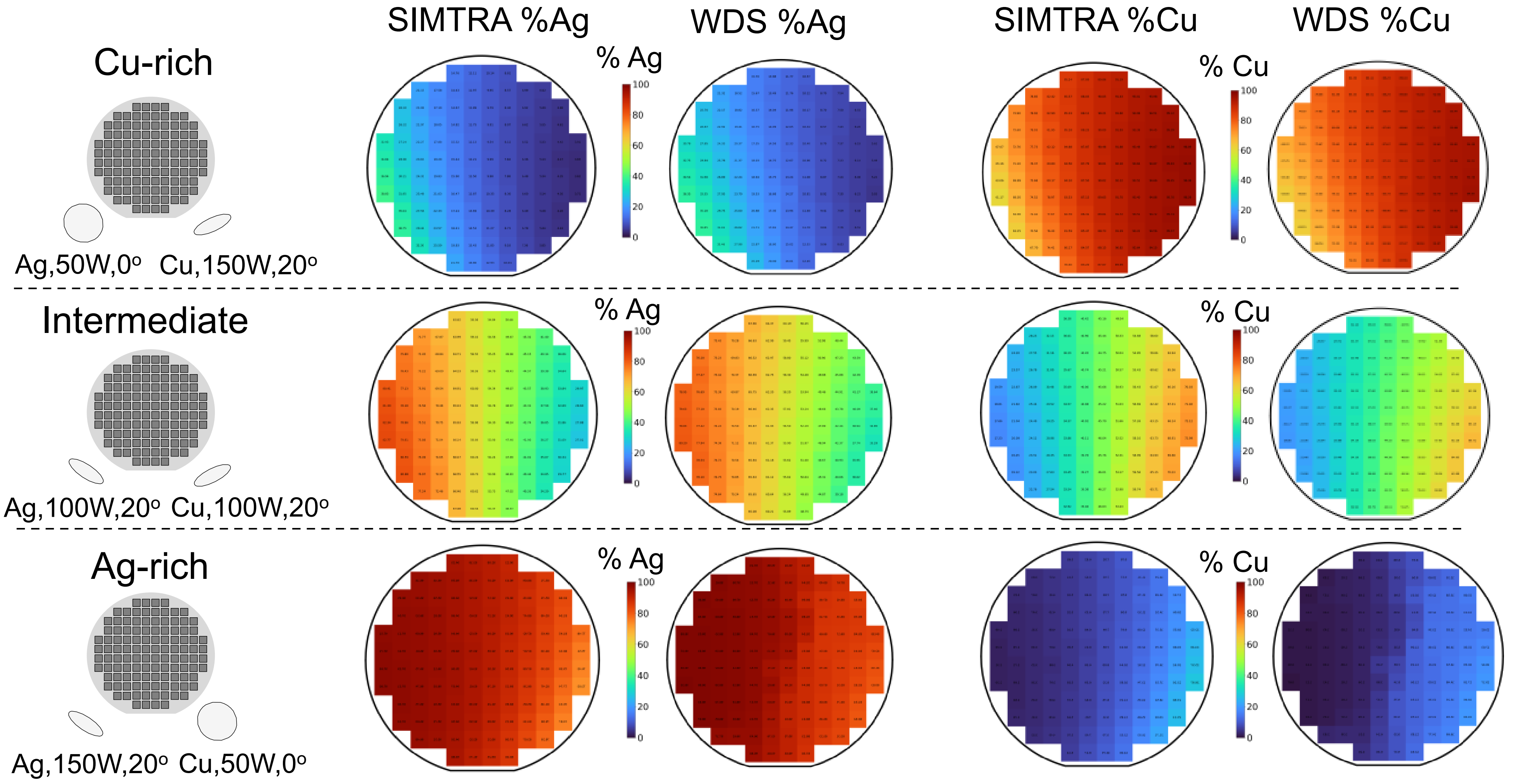
- Benefits:
  - 112 depositions would take more than a month of non-stop pumping and sputtering!
  - Photolithographic techniques can potentially create many more samples per wafer.

- Limits:
  - The samples created this way have many process conditions in common.
  - Composition is not the only gradient across the wafer.
  - Requires planning ahead via calibration or simulation for best benefit.

↓

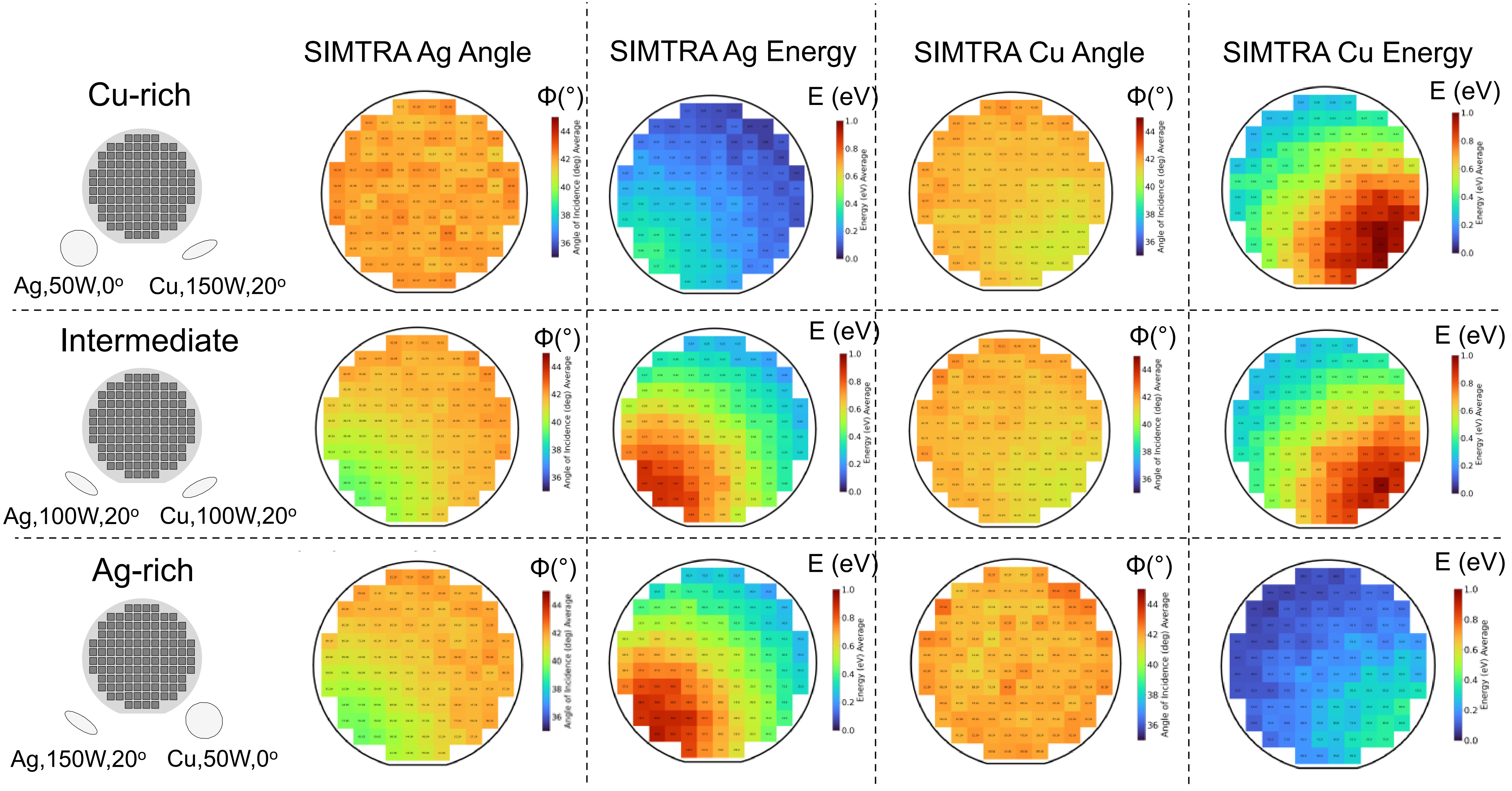
SIMTRA: SImulation of Metal TRAnsport

SIMTRA-predicted compositions closely match values measured by Wavelength Dispersive Spectroscopy (WDS)



Results demonstrate how three combinatorial depositions can span nearly the full range of binary composition when utilizing varied sputter power and gun tilt angle.

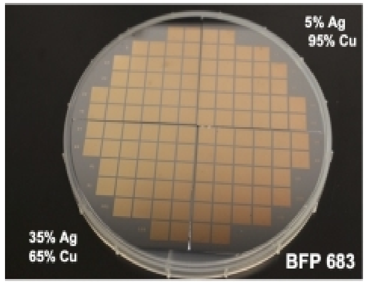
SIMTRA-simulations of Sputtering Atom Energy and Angle of Incidence



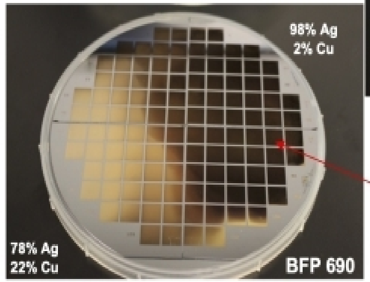
Thermal and Chemical Instability

- Nanocrystalline materials are subject to loss of nanocrystalline properties if grain growth is not mitigated.
- Oxidation is a concern, but for Ag-rich compositions of Cu-Ag, sulfur tarnishing is a far more serious effect.
- There's a very clear compositional dependence for tarnishing.

Graded Cu-Ag, copper rich

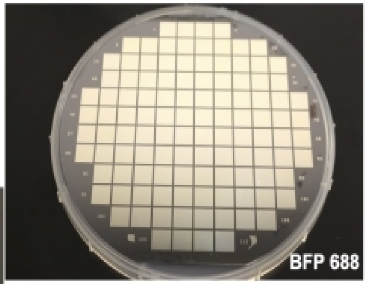


Graded Cu-Ag, silver rich

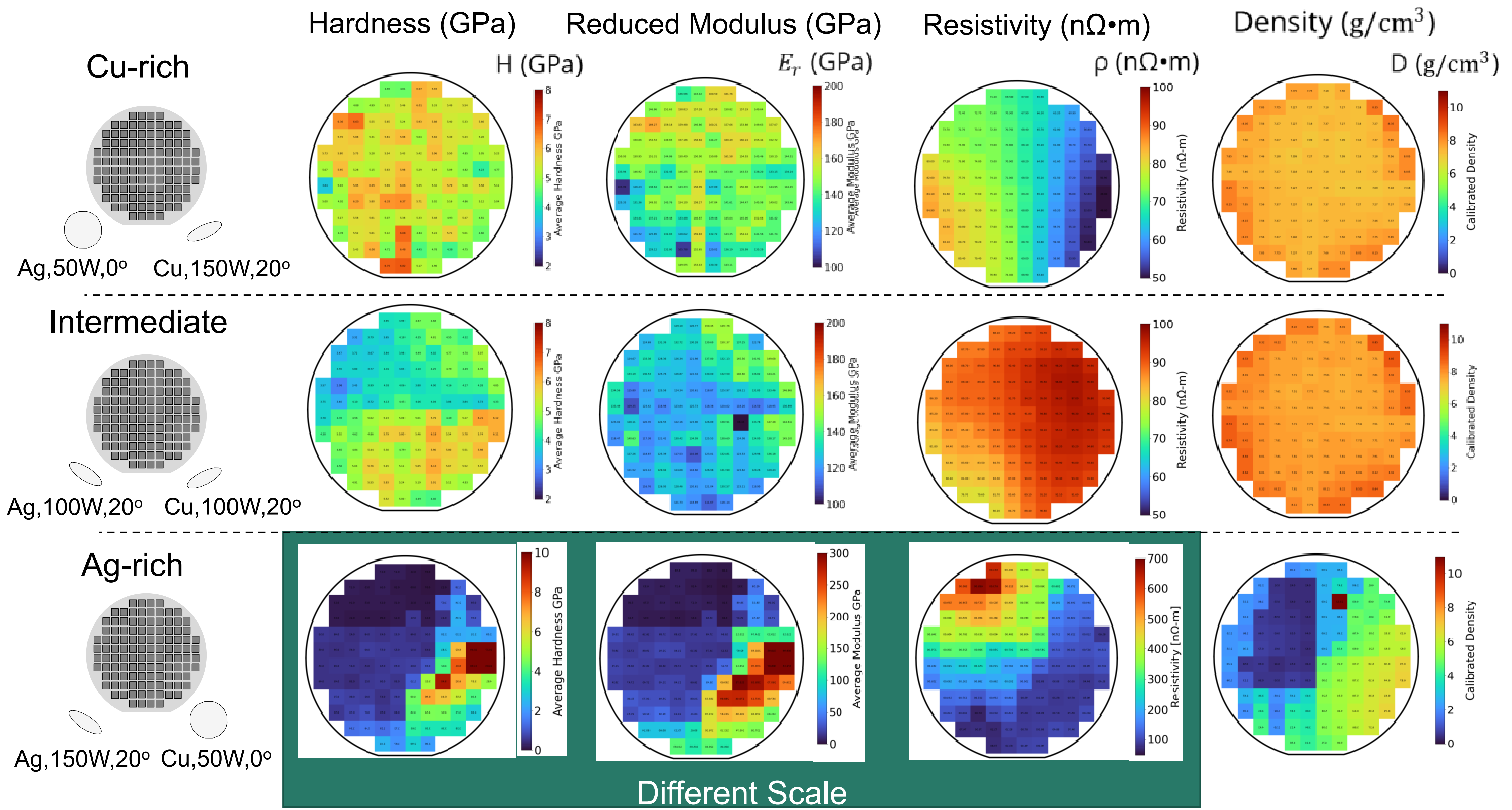


Tarnished within 1 week after deposition

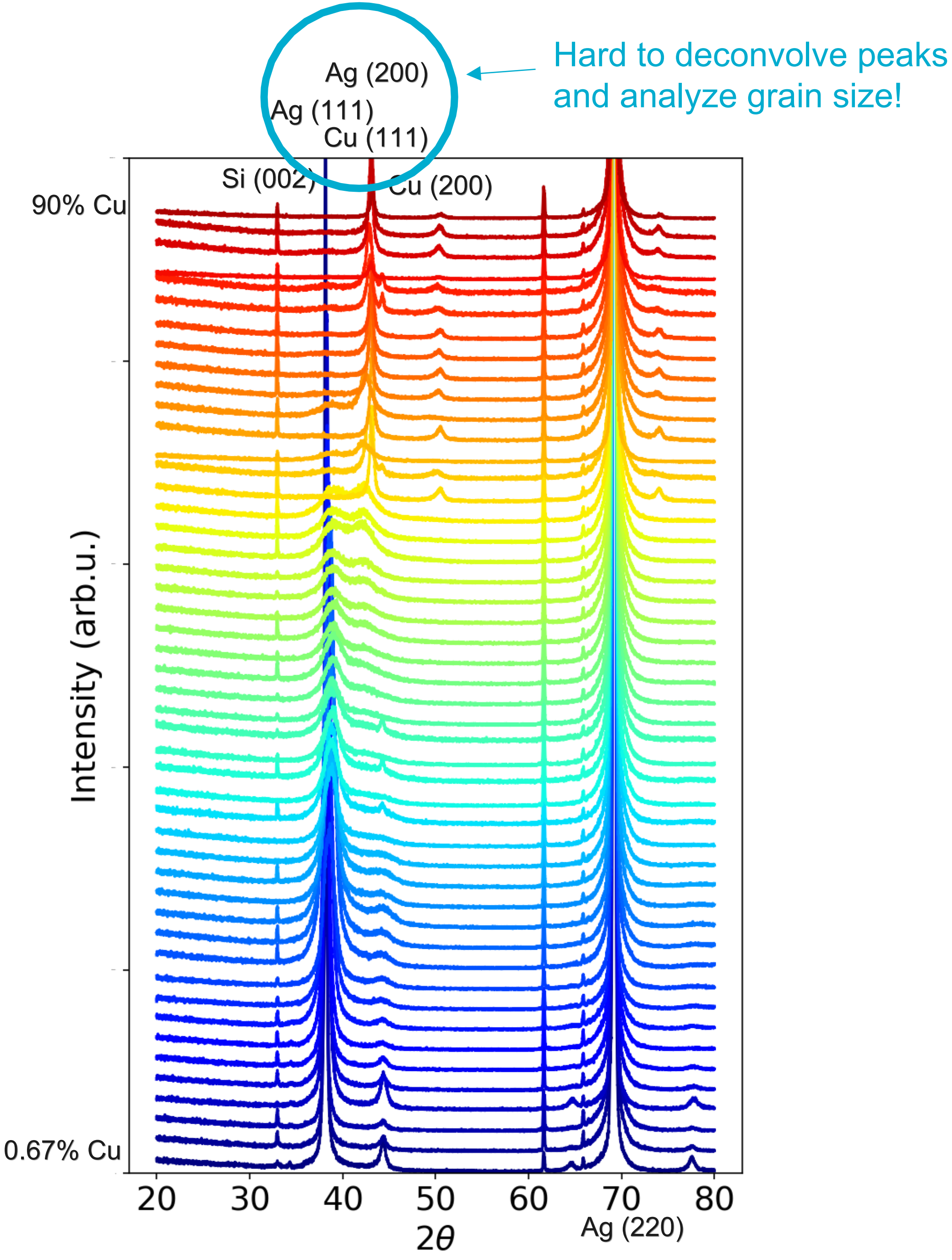
Pure Ag – minimal tarnishing



High Throughput Property Measurements



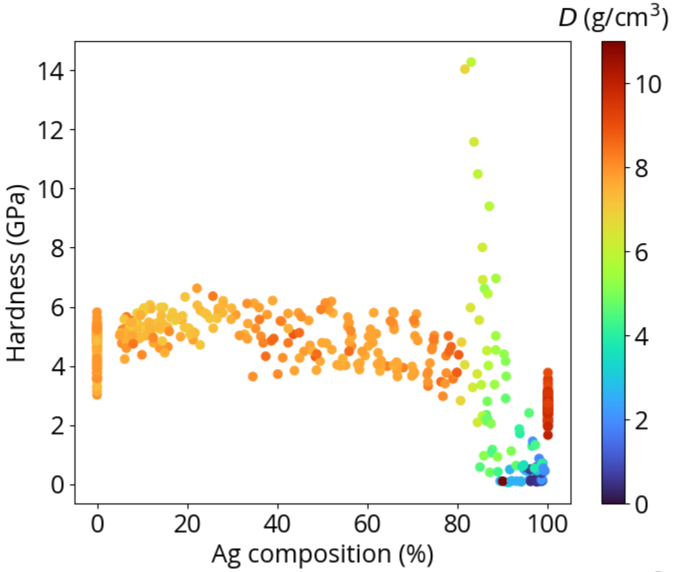
Measurements and Modalities to Improve

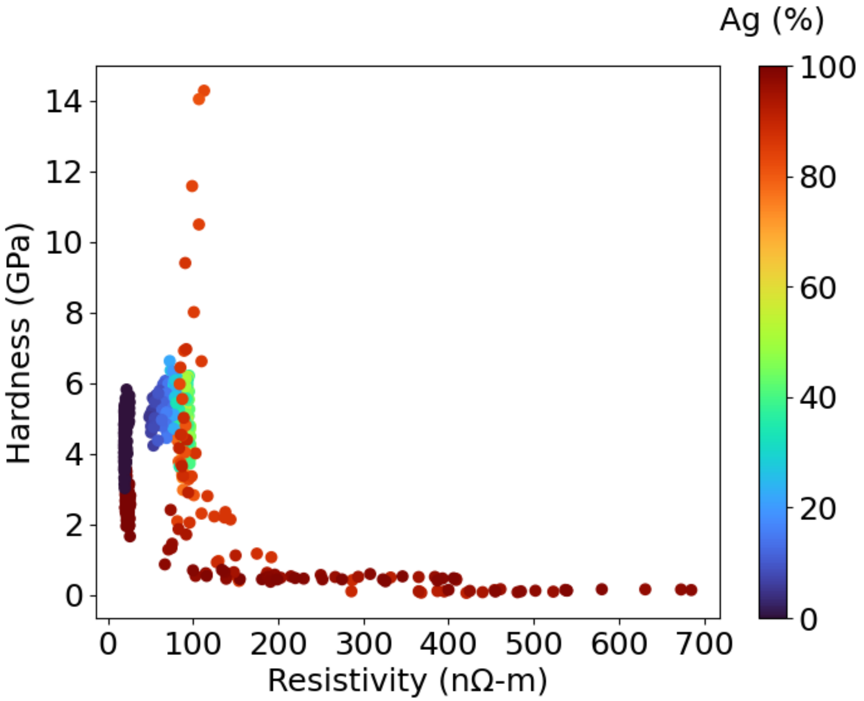


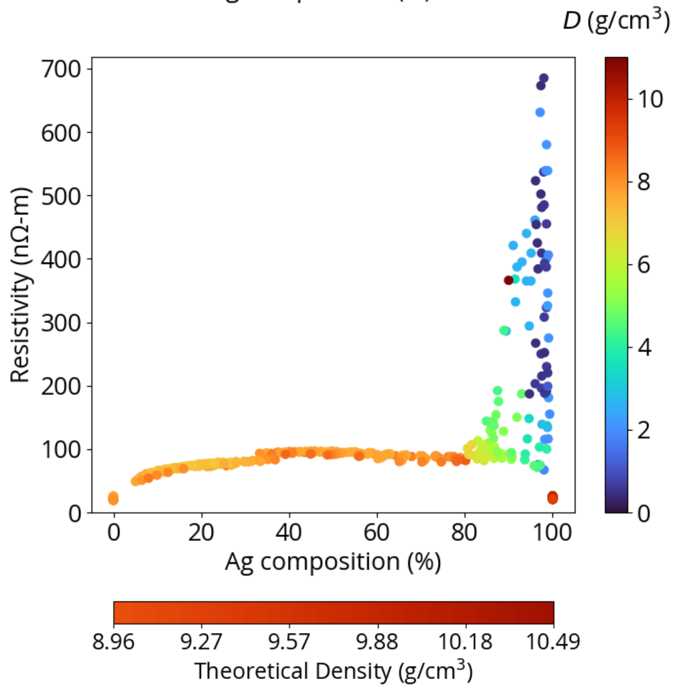
- XRD data acquisition is automated.
- Should provide information on grain size and orientation.
- But analysis may be nontrivial!
- Other structural analysis tools are very powerful, but too slow to call high-throughput:
  - RBS
  - SEM
  - TEM

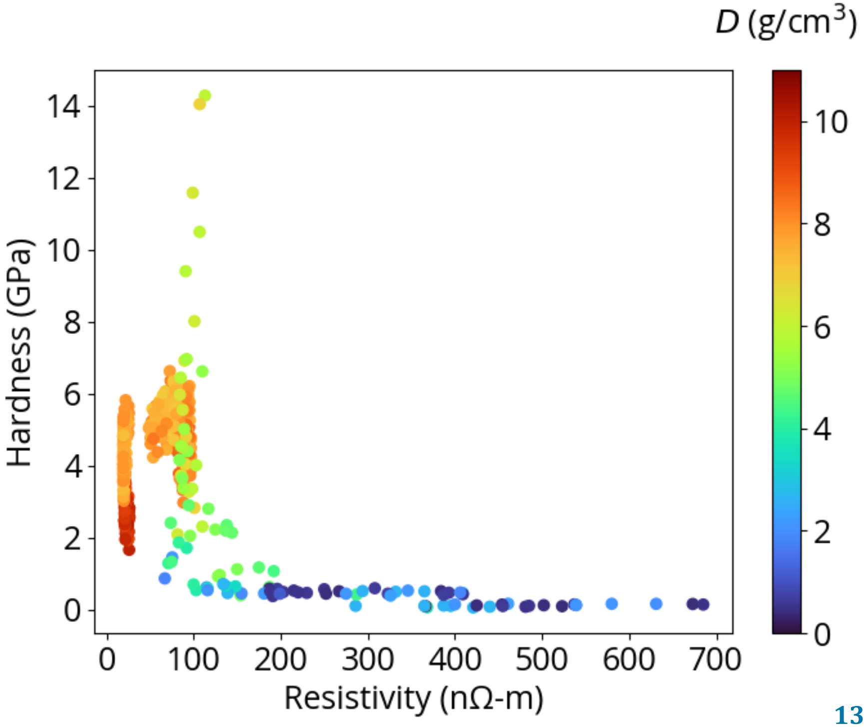
Optimization of Cu-Ag

- Goals:
  - Low resistivity
  - High hardness
  - Chemically stable composition
  - Stably nanocrystalline
- Issues:
  - Forms a eutectic
  - Reacts with atmosphere
  - Few depositions = survey few process conditions
- Recommendations:
  - High density
  - Cu-rich composition



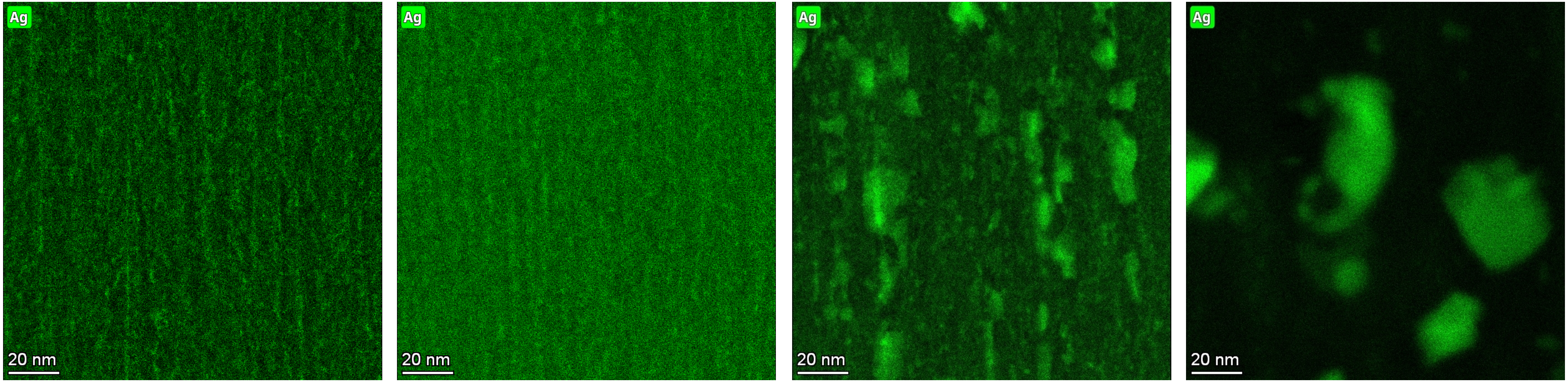






Cu-Ag (6%) Treatment Comparisons

No Bake | 100°C | 200°C | 300°C

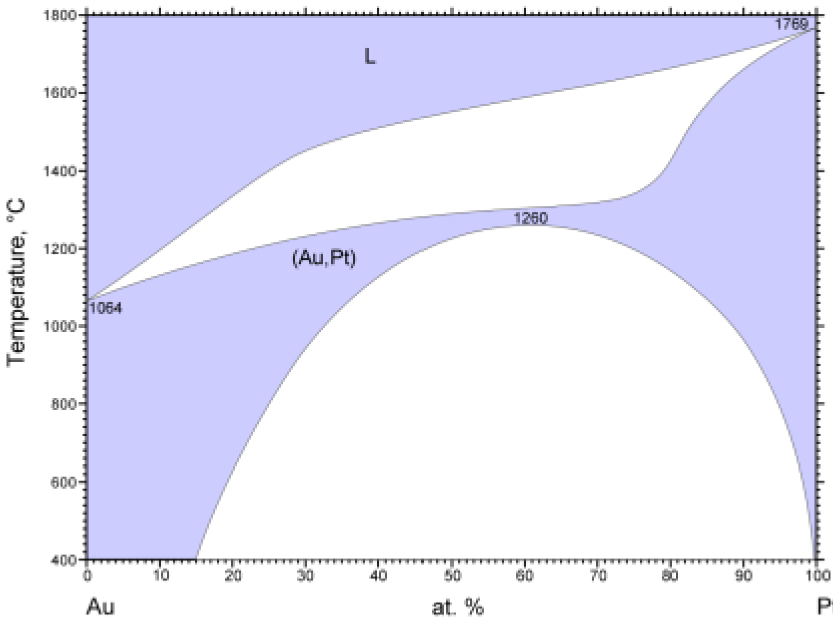


- Signs of weak Ag segregation to the grain boundaries in the as-deposited condition.
- Application of heat to the depositions caused phase separation at and above 200°C.
- At 300°C the deposition underwent grain growth and transitioned to an equiaxed structure.

Ni-Pt

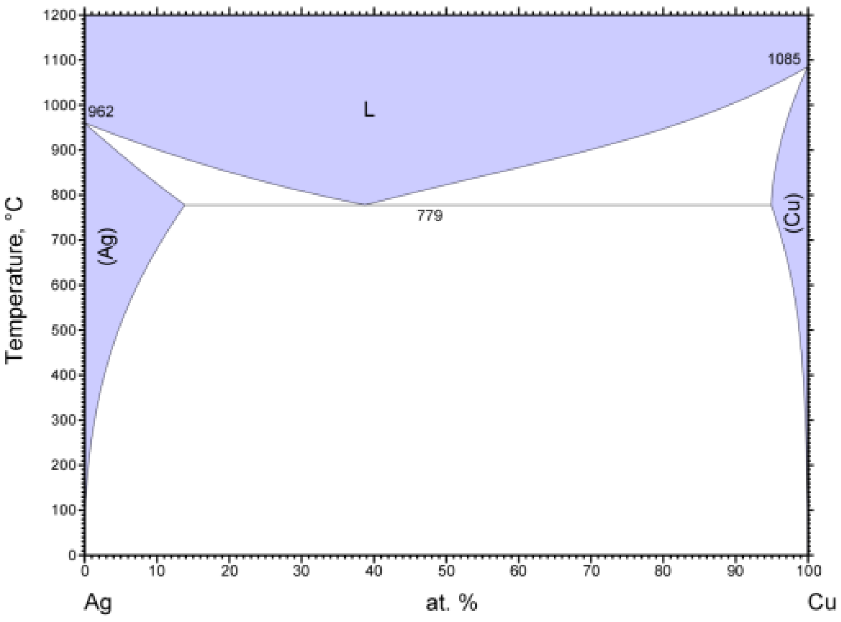
- Ni-Pt has a phase diagram more in line with Pt-Au, but is substantially cheaper.
- Brings new challenges: Ni is ferromagnetic and can oxidize.
- Ni is less massive than Pt or Au, and behaves differently during the sputtering process.

Au-Pt



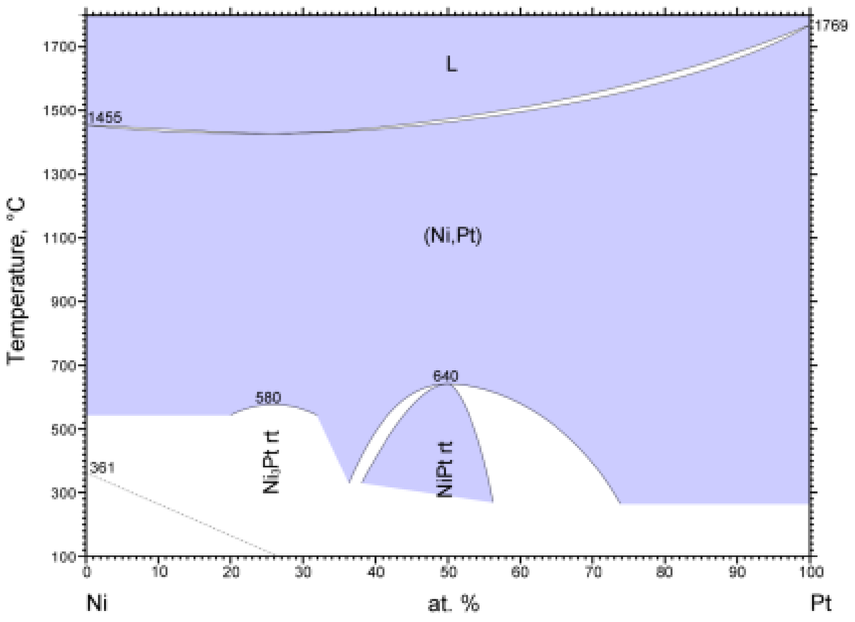
Okamoto H., and Massalski T.B., Au-Pt (Gold-Platinum), Binary Alloy Phase Diagrams, II Ed., Ed. T.B. Massalski, Vol. 1, 1990, p 414-416

Cu-Ag



Cao W., Chang Y.A., Zhu J., Chen S., and Oates W.A., Thermodynamic modeling of the Cu-Ag-Au system using the cluster/site approximation, Intermetallics, Vol. 15, 2007, p 1438-1446

Ni-Pt

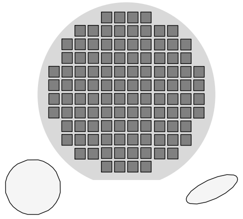


Nash P., and Singleton M.F., Ni-Pt (Nickel-Platinum), Binary Alloy Phase Diagrams, II Ed., Ed. T.B. Massalski, Vol. 3, 1990, p 2841-2845

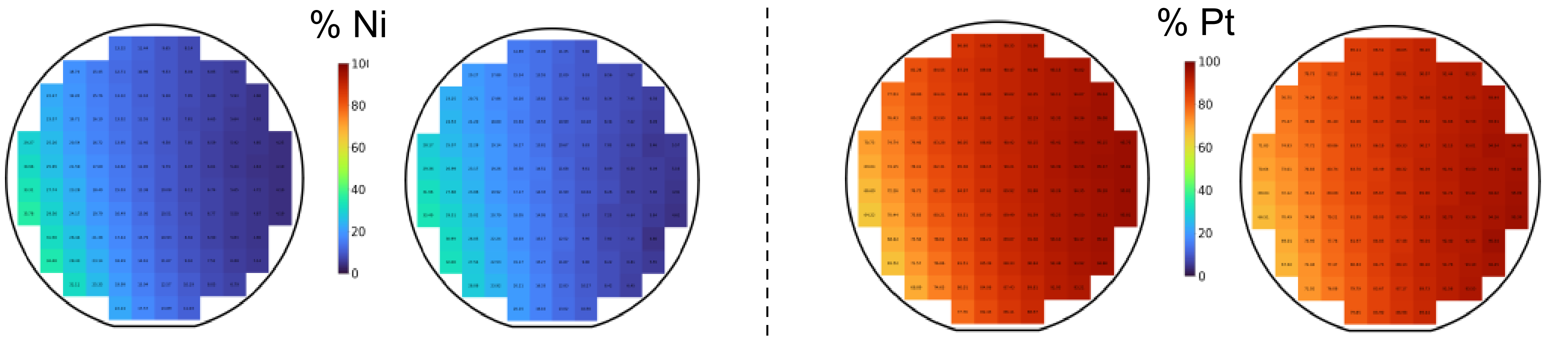
SIMTRA-predicted and WDS composition for Ni-Pt

SIMTRA %Ni | WDS %Ni | SIMTRA %Pt | WDS %Pt

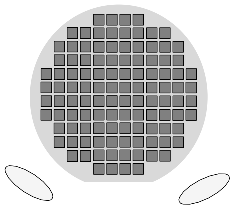
Pt-rich



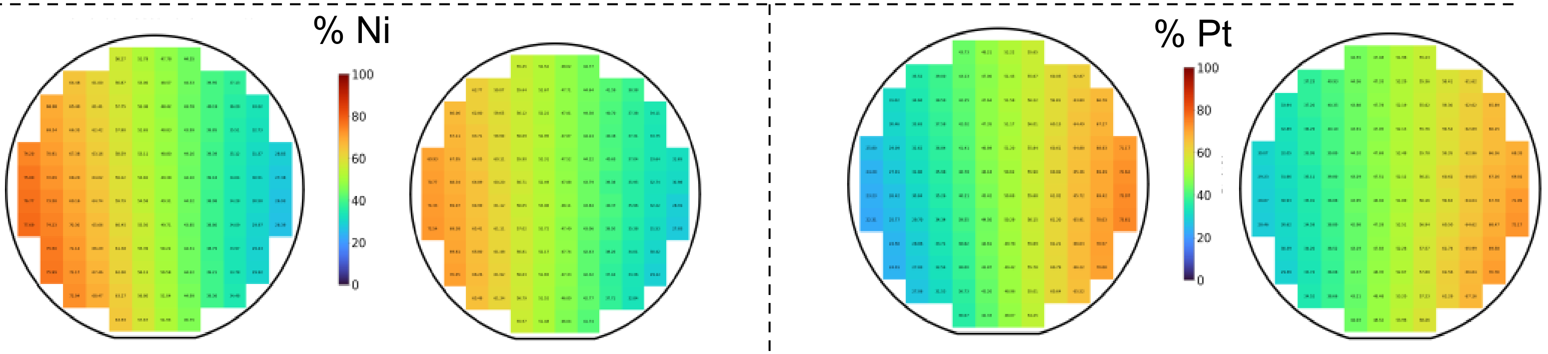
Ni,50W,0° Pt,150W,20°



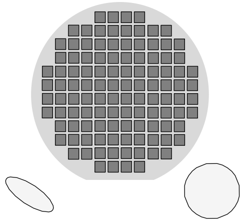
Intermediate



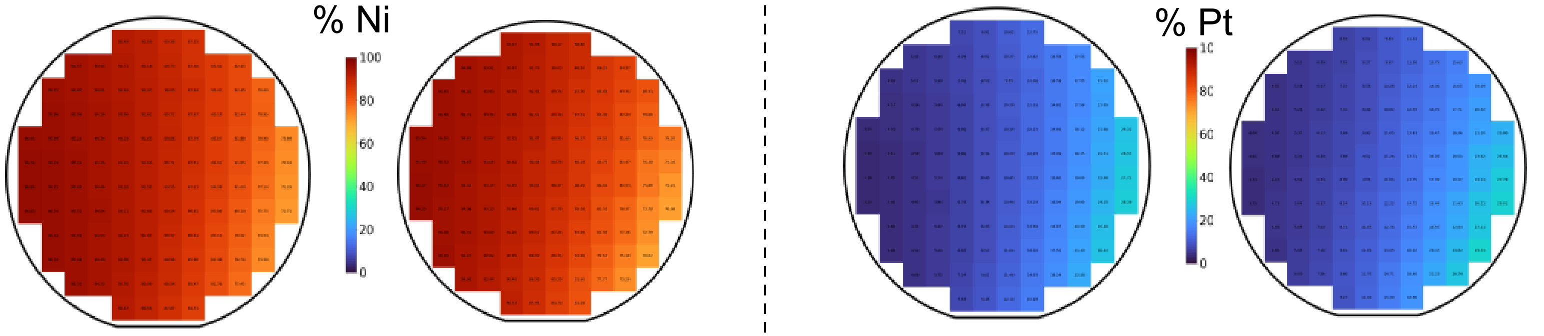
Ni,100W,20° Pt,100W,20°



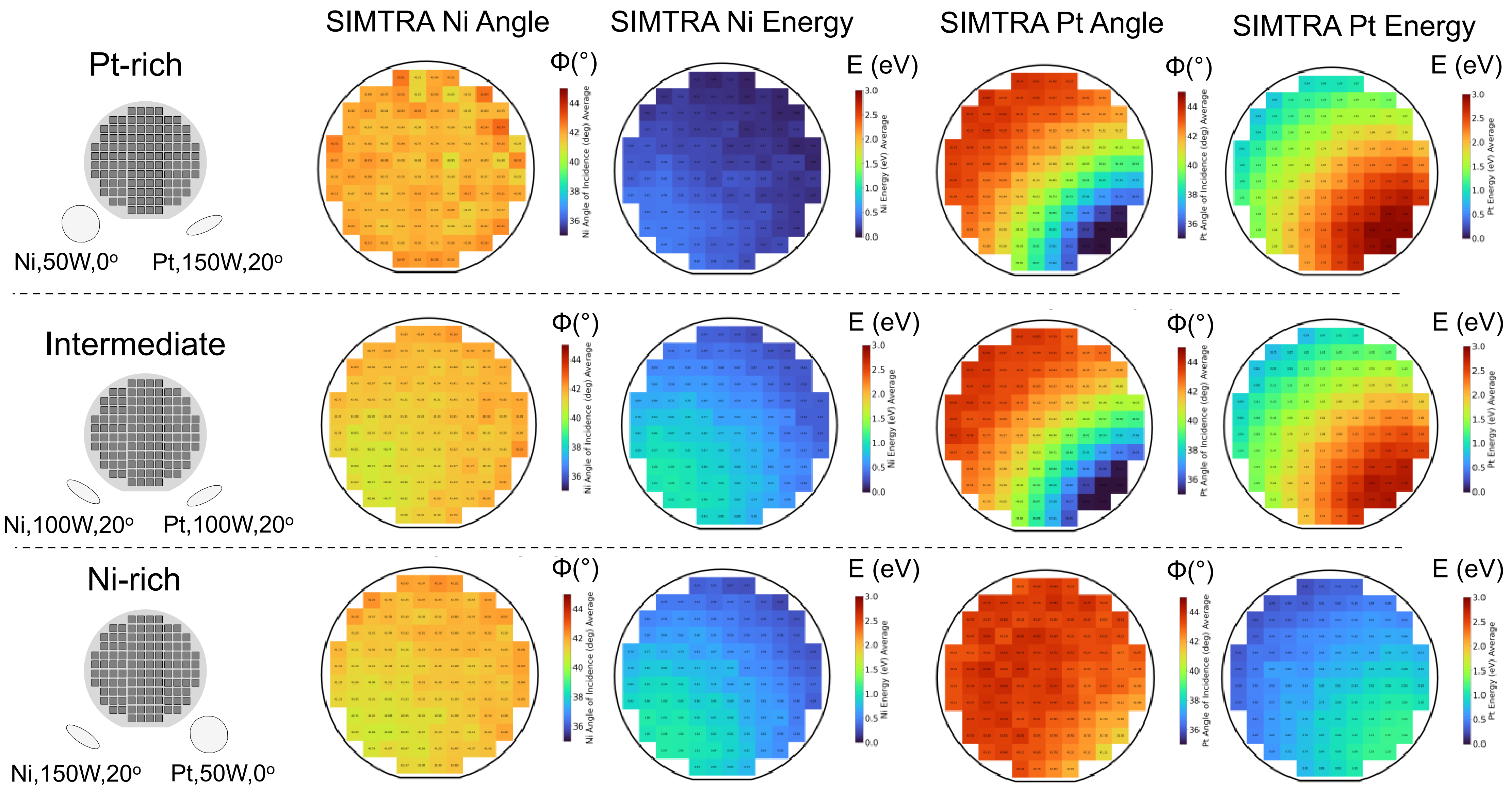
Ni-rich



Ni,150W,20° Pt,50W,0°



Ni-Pt: SIMTRA-predictions of Energy and Angle of Incidence



Conclusions

- By simple modifications of standard confocal sputter deposition techniques, a small set of wafers can survey property and structural variation across nearly the full compositional range.
- Deposition of that compositional range can now occur substantially *faster* than measurement and analysis of those films.
  - 1 wafer deposited lead to 112 samples!
- Seeking optimized material properties for non-noble binaries contends with, and reveals trends of, atmospheric reactivity.
  - Not all materials are equal. Cu-Ag is interesting, Ni-Pt may be more practical!
- SIMTRA provides a foothold for connecting fabrication conditions to structure and properties of resulting films, but cannot currently reverse engineer optimal process parameters for optimal films.

Acknowledgements

Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC (NTESS), a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration (DOE/NNSA) under contract DE-NA0003525.

This written work is authored by an employee of NTESS. The employee, not NTESS, owns the right, title and interest in and to the written work and is responsible for its contents.

Any subjective views or opinions that might be expressed in the written work do not necessarily represent the views of the U.S. Government. The publisher acknowledges that the U.S. Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this written work or allow others to do so, for U.S. Government purposes.

The DOE will provide public access to results of federally sponsored research in accordance with the DOE Public Access Plan.

This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science.

The authors acknowledge funding under the *Beyond Fingerprinting* Sandia Grand Challenge Laboratory Directed Research and Development (GC LDRD) program.